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TEXTILE RESEARCH JOURNAL

VOL. XX, NO. 2 February, 1950

Microbiological Deterioration of Cellulose During the First 72 Hours of Attack*

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Introduction

The effects of microbiological attack on breaking strength of textiles have been studied in many laboratories. In most cases a great loss of strength was noted after 3 days of attack by molds. A preliminary study in this laboratory of the course of attack by 3 organisms during the first 72 hrs. indicated that the strength of cotton duck was reduced from 35% to 66% during this time, although there was no evidence of mycelium to the unaided eye.

This project was undertaken to study further the profound changes which take place in cellulosic fibers due to the action of 5 cellulolytic molds during the first 72 hrs.

The original proposal contemplated the study of this breakdown by established methods and by a number of new ones. After the work had got under way some of these methods did not appear to be feasible or useful and were replaced by other methods.

The work done on the present project included: (1) a study of the strength loss of textiles due to the growth of 5 molds; (2) a study of the microscopic appearance and chemical resistance of fibers after attack by mildew; (3) a study of the growth of cellulolytic molds on modified celluloses and on sugars; (4) attempts to measure the initial decomposition products; and (5) a study of the effects of enzymes of *Chaetomium globosum* on several forms of cellulose.

Experimental Data

1. Effect of 5 Cellulolytic Organisms on Cotton Duck During the First 72 Hrs. of Incubation

In a previous publication [12] 5 cellulolytic organisms were compared with regard to their effect on the strength and weight of 8-oz. unbleached, unsized cotton duck. Residual strength was determined by making breaking-strength determinations each day of incubation up to complete destruction of the

* This project was sponsored by the Office of Naval Research under Contract and Task Number N8ONR554 and Project Designation Number NRO34-244, and the work was carried on at the Institute of Textile Technology, Charlottesville, Virginia.

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fabric specimens. The first specimens were removed from incubation after the first indications of growth were visible to the unaided eye. This was usually after from 2 to 4 days, depending upon the organism.

These experiments were extended to include the effect of these same 5 organisms during the period before visible evidence of growth.

Materials and Methods.—The 5 fungi used in this experiment were the same as those reported in "Microbiological Deterioration of Textiles: I: Comparison of Five Cellulolytic Fungi" [12]. These fungi and their identifying strain numbers are as follows:

ITT No.	Name of fungus	USDA No.
14	*Thielavia* sp.	46
15	*Humicola* sp.	91
16	*Chaetomium globosum*	1042.4
17	*Stemphylium* sp.	1203.1
18	*Myrothecium verrucaria*	1334.2

To provide spores for the experiments, the organisms were grown for 14 days at 29°C on filter-paper slants.

Deterioration of the breaking-strength specimens of cotton duck was carried out in 16-oz. square, screw-cap bottles, according to the method of Greathouse *et al.* [10]. The cap of each bottle was fitted with a glass-fabric insert which covered a hole in the cap. Into each 16-oz. bottle was poured 35 ml. of molten salts-agar medium (see Table I) and the bottles were capped. They were then sterilized at 15-lb. pressure and 121°C. After sterilization, the bottles were placed on their sides to allow the agar to harden.

Strips of 8-oz. duck, 5 in. × 1½ in., with the warp in the long direction, were also sterilized, and after the agar had hardened, a strip of fabric was placed, aseptically, on the agar in each bottle. For each organism 240 bottles were thus prepared. (This figure is obtained by multiplying the number of specimens for each point on the curves [10] by the number of incubation periods from 3 hrs. to 72 hrs. [24].)

The inoculum for each organism was prepared by adding the spores from 5 culture tubes to 500 ml. of sterile distilled water. Two ml. of an inoculum were pipetted uniformly over the strips in each of the 240 bottles. The bottles were then incubated at 29°C for from 3 to 72 hrs. Controls consisted of similar fabric strips incubated in contact with the salts-agar medium, but not inoculated with fungal spores.

TABLE I. COMPOSITION OF CULTURE MEDIUM

Component	Amount	Component	Amount
NH_4NO_3	3.0 g.	$MgSO_4 7H_2O$	2.0 g.
KH_2PO_4	2.5 g.	Agar	18.0 g.
K_2HPO_4	2.0 g.	Water	1.0 l.

After each succeeding 3-hr. period of incubation, 10 specimens for each organism were removed from the bottles, washed, dried, raveled to 1 in. in width, and then conditioned at 65% R.H. and 72°F before breaking on a Suter Fabric Tester. Loss of strength was calculated as percent residual strength.

Results.—Prior to the 48th hour of incubation, no sign of growth was seen with the unaided eye. At about the 48th hour of incubation faint traces of mycelium were evident in the case of *Thielavia* sp., *Humicola* sp., and *Chaetomium globosum*. *Myrothecium verrucaria* showed yellow spots at about the 60th hour, whereas *Stemphylium* sp. did not show evidence of growth until the 120th hour. Because of the fact that *Stemphylium* sp. grows at a slower rate than the other organisms, the incubation period was extended to 120 hrs., and samples were taken every 6 hrs.

Strength Tests.—The figures which appear in Table II were obtained from averages based on 10 determinations for each 3-hr. period. From the values were calculated the percentages of residual strengths based on the strength of the control fabric.

The data in Table II were plotted and smooth curves were drawn, as shown in Figures 1–5.

The data show that microbiological damage, as evidenced by loss in strength, takes place much sooner than is usually suspected and before the mycelium can be detected by the unaided eye. Four of the organisms show a definite lag in effect, which appears to correspond to the germination period for each organism. For *Humicola* sp. it lasts about 18 hrs., for *Chaetomium globosum* about 9 hrs., for *Myrothecium verrucaria* about 18 hrs., and for *Stemphylium* sp. about 36 hrs. *Thielavia* sp. does not seem to have such a lag, inasmuch as the strength of the inoculated fabric begins to drop off after the 3rd hour of incubation.

Undoubtedly, there must be great variation in these results because the breaking strengths of the relatively few fibers which have been attacked at this early stage may be offset by the large number of fibers which have not been attacked. Therefore, it would seem that the chief value of this experiment

lies in the qualitative demonstration that microbiological damage can take place very soon after incubation has started, under ideal conditions of growth.

This work suggested that a study of single fibers, rather than of fabrics, would be more apt to produce pure, "undiluted" results.

The next experiment was based on this conclusion.

2. Study of Mildewed Fibers in Dilute Alkali

With regard to the determination of microbiological damage in cellulosic fibers by microscopic methods, Marsh [15] reviews the literature as follows:

"Of the various methods which might be used in detecting and diagnosing microbiological fiber and textile deterioration, the most attention has been paid to certain microscopic techniques. Fleming and Thaysen found that when damaged cotton fibers are subjected to the carbon disulfide-sodium hydroxide swelling technique originally described by Balls they show a decreased tendency toward the beading phenomenon which occurs so strikingly with normal fibers. A similar observation had been made previously by Carbone on microbiologically damaged fibers swollen in Schweitzer's reagent. Fibers damaged by microorganisms are also stated by Fleming and Thaysen to exhibit numerous cracks and incisions when tested by their method. Denham criticizes the swelling technique of Fleming and Thaysen as a diagnostic method for indicating microbiological damage on the ground that the reaction is dependent only on the behavior of the cuticle and that 'slight mechanical damage to the cuticle, such as occurs in ginning, will produce fallacious results, while an organism which does not affect the cuticle, however extensive its ravages in the lumen and the wall layers, may escape observation.' According to Bright, Thaysen in later conversation placed emphasis on the appearance of cracks and crevices in the swollen fibers as well as on the presence or absence of the beading phenomenon. He has himself described another microscopic method for detecting fiber damage to cotton. His method again is apparently essentially a measure of the condition of the primary wall. It involves treatment of the fibers with 11% sodium hydroxide, then with a Congo red solution, and finally with 18% sodium hydroxide. The first, milder swelling is intended to rupture the primary wall of damaged but not of undamaged fibers, subsequent treatment with Congo red staining the underlying cellulose at these ruptured points. Final swelling in 18% sodium hydroxide brings about more extensive rupture of the cuticle and exposure of unstained cellulose. Clegg presents several photomicrographs showing the results of tests on variously damaged cotton fibers by use of the Congo red test. Prindle has used a combination swelling-staining technique with cuprammonium solution and Victoria blue stain for detection of mildew damage to cotton fibers."

In the course of surveying the field for possible methods of determining microbiological damage in single fibers, the Clegg [4] Congo red test was investigated. The Clegg technique involves the swelling and staining of tufts of fibers in a mass. From this mass individual fibers are selected for microscopic study.

However, in our work we examined microscopically individual fibers which had been mildewed for a given time. While using the Clegg technique on a single fiber which had been mildewed for 24 hrs., with constant observation under the microscope, it was found that alkali alone, without dye, revealed profound, localized changes in the fiber. This original observation was made with the use of 11% NaOH. The fiber had been mounted in water, and except for the presence of spores and mycelium of *Chaetomium globosum* it appeared to be a sound fiber. Then, by using a bit of blotting paper, the water under the cover slip was withdrawn from one side and 11% NaOH was introduced by pipet from the opposite side. By constantly scanning the whole fiber, a small section was seen to dissolve away. This can be seen in Figure 6.

This observation stimulated the following experiment.

Materials and Methods.—Cotton fibers taken from card sliver, of about $1\frac{1}{16}$ in. average length, were first treated to remove waxy material. Wax was removed by refluxing in alcohol for 6 hrs., followed by refluxing in ether for 6 hrs.

In a preliminary experiment the fibers were cemented on a card with a 1-in. opening so that 1 in. of fiber was available for attack by *Chaetomium globosum*. These cards were then placed on mineral salts-agar in petri dishes and were incubated for 3-hr. periods up to 72 hrs. Up to 24 hrs. all the fibers remained intact. However, after the 24-hr. period an increasing number of fibers were lost because of breakage at weak points. This breakage appears to be due to the brittleness of the fibers. Denham [5] lists brittleness as a characterizing feature of partly degraded cotton fibers.

This method was later abandoned and the following one was adopted:

Sterile molten mineral salts-agar was placed on sterile microscope slides in such a manner that a thin film of agar medium large enough to support a complete cotton fiber was directly in the center of each slide. When the agar had hardened, a single cotton fiber was placed on the agar and was inoculated with *Chaetomium globosum*. After incubation

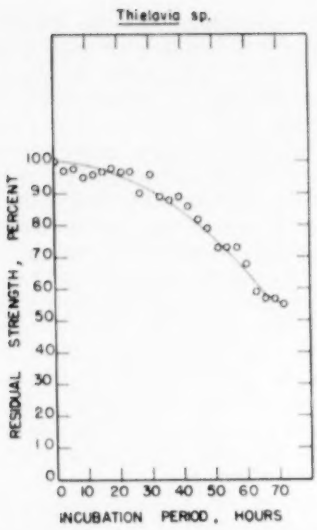

FIG. 1. *Relationship between time of incubation and residual strength of cotton duck attacked by* Thielavia *sp. (Based on data of Table II.)*

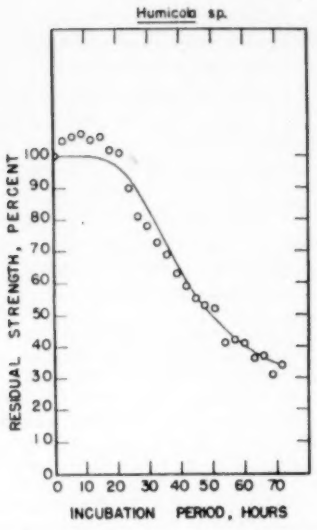

FIG. 2. *Relationship between time of incubation and residual strength of cotton duck attacked by* Humicola *sp. (Based on data of Table II.)*

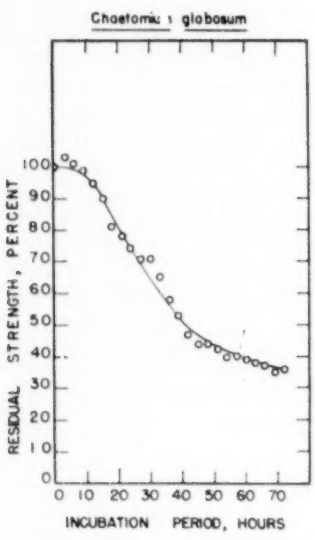

FIG. 3. *Relationship between time of incubation and residual strength of cotton duck attacked by* Chaetomium globosum. *(Based on data of Table II.)*

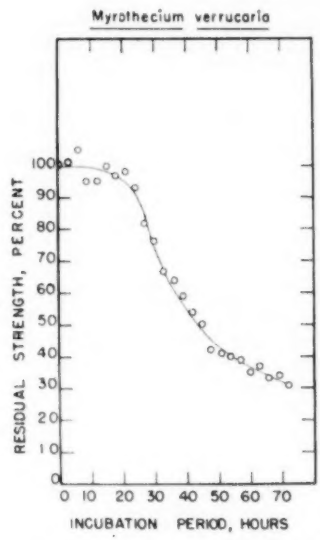

FIG. 4. *Relationship between time of incubation and residual strength of cotton duck attacked by* Myrothecium verrucaria. *(Based on data of Table II.)*

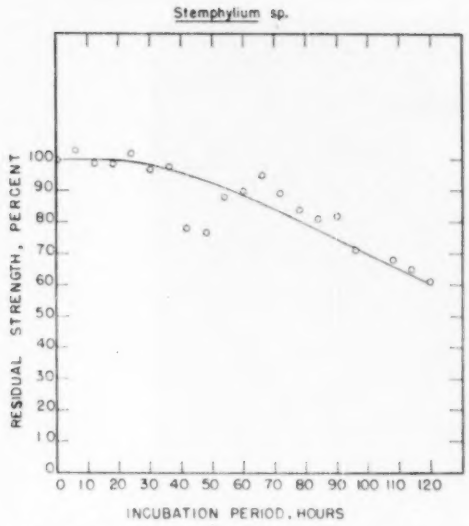

FIG. 5. *Relationship between time of incubation and residual strength of cotton duck attacked by* Stemphylium *sp. (Based on data of Table II.)*

for from 12 to 72 hrs., a large number of fibers on slides were removed at each successive 12-hr. period and were treated with varying concentrations of alkali. For each concentration of alkali, 10 fibers on slides were examined. The fibers were first examined by placing a drop of distilled water over each fiber and then covering it with a cover slip. After examination of the specimen at a magnification of 430 times, the water was removed with blotting paper from one edge and the proper concentration of alkali was introduced under the cover slip from the opposite edge. A period of 10 min. was usually sufficient to produce the effects listed in Table III. The values in the table are averages for 10 determinations in each case.

A graphic representation of the data in Table III is given in Figure 8.

Here we have further evidence that cotton fibers are seriously damaged by molds at a relatively early stage of incubation. After only 12 hrs. of incubation with *Chaetomium globosum*, treatment with 9% NaOH revealed an average of one hole per fiber. Treatment with 11% NaOH increased this value to 3 holes per fiber. After 24 hrs. of incubation an average of one hole per fiber could be seen when the fiber was mounted in water; this was the earliest

TABLE II. RESIDUAL STRENGTH OF 8-OZ. DUCK ATTACKED BY 5 DIFFERENT FUNGI, CALCULATED AS PERCENTAGE OF STRENGTH OF THE CONTROL FABRIC

Hrs. of incubation	*Thielavia*	*Humicola*	*Chaetomium*	*Myrothecium*	*Stemphylium*
3	97	105	103	101	—
6	98	106	101	105	103
9	95	107	99	95	—
12	96	105	95	95	99
15	97	106	90	100	—
18	98	102	81	97	99
21	97	101	78	98	—
24	97	90	74	93	102
27	90	81	71	82	—
30	96	78	71	76	97
33	89	73	65	67	—
36	88	69	58	64	98
39	89	63	53	59	—
42	86	59	47	54	78
45	82	55	44	50	—
48	79	53	44	42	77
51	73	52	42	41	—
54	73	41	40	40	88
57	73	42	40	39	—
60	68	41	39	35	90
63	59	36	38	37	—
66	57	37	37	33	95
69	57	31	35	34	—
72	55	34	36	31	89
78	—	—	—	—	84
84	—	—	—	—	81
90	—	—	—	—	82
96	—	—	—	—	71
102	—	—	—	—	49
108	—	—	—	—	68
114	—	—	—	—	65
120	—	—	—	—	61

period at which holes could be seen when the fiber was mounted in water.

The number of holes increased slowly during the 48-hr. period, even when the fibers were treated with 11% NaOH. However, beginning with the 48-hr. stage there was an increase in the number of holes at all concentrations of alkali. Also at this stage the appearance of the swelled fiber was different from that at the 24-hr. stage. Figure 6 shows the appearance of the single notch of a 24-hr. fiber, whereas Figure 7 shows the badly disintegrated appearance of a 48-hr. fiber. In both cases the disintegrated regions are highly localized. A few qualitative tests of the growth of *Chaetomium globosum* on viscose rayon showed an entirely different pattern of attack on the surface of the filaments.

This localized action of molds such as *Chaetomium globosum* on cotton fibers tends to explain several paradoxes. First, the great loss in strength of cotton

FIG. 6. *Micrograph of a fiber which had been incubated for 24 hrs. with* Chaetomium globosum *and treated with NaOH. A single notch (alkali-soluble part of the fiber) can be seen.*

FIG. 7. *Micrograph of a fiber which had been incubated for 48 hrs. with* Chaetomium globosum *and treated with NaOH. The fiber is badly disintegrated.*

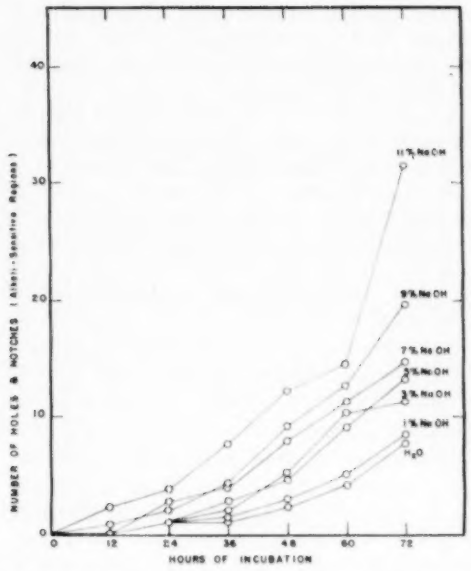

FIG. 8. *Relationship of mildew damage of cotton fibers to solubility in various concentrations of NaOH.*

fabric with comparatively little loss in weight can be explained on the basis of the relatively small amount of cellulose which is removed from each fiber by microbiological action. This conclusion may be questioned, however, on the ground that notches and holes are not readily apparent until after treatment with alkali, at least during the early stages of incubation. The following experiment was planned to test the validity of this hypothesis.

Cotton fabric strips, similar to those used in previous breaking-strength studies, were incubated with *Chaetomium globosum* for periods of 12, 24, 48, and 72 hrs. For each time period there were 20 specimens. After each incubation period 10 strips in each group were conditioned and broken, and the other 10 were treated with 11% NaOH for 30 min. on a reciprocal shaker, and were then washed until free of alkali. After conditioning they also were broken. In addition, 20 strips of unmildewed control fabric were treated similarly. The results appear in Table IV.

That there is no significant difference in breaking strength between specimens which have been broken immediately after incubation with *Chaetomium globosum* and those which have been given an additional treatment with 11% NaOH is shown in Table IV. These data may be interpreted in the following manner: The holes and notches observed in mildewed fibers after treatment with alkali certainly must contribute to the loss in strength of these fibers, but since there is no change in the strength of mildewed fibers after treatment with alkali, then the alkali-soluble regions must be the cause of the loss of strength even before the treatment with alkali.

A second paradox is the fact that the cuprammonium fluidity of mildewed cotton, as reported by various workers, does not change appreciably from that of the original value. A possible explanation for this is that only a small amount of cotton fiber is attacked by the molds.

The conversion of native cotton cellulose into alkali-soluble cellulose by the enzymes of *Chaetomium globosum* may be the result of hydrolysis of the 1,4-glucosidic linkages. This is analogous to the degradation of cellulose by mineral acids. It is the commonly accepted theory that the degradation of cellulosic materials by acids takes place by a progressive

TABLE III. RELATIONSHIP OF GROWTH OF *Chaetomium globosum* ON COTTON FIBERS TO SOLUBILITY IN VARIOUS CONCENTRATIONS OF SODIUM HYDROXIDE, AS DETERMINED BY THE NUMBER OF HOLES AND NOTCHES (ALKALI-SOLUBLE REGIONS) OBSERVED

Hrs. of incubation	Average no. of holes and notches observed for 7 concentrations of alkali						
	0%	1%	3%	5%	7%	9%	11%
0	0	0	0	0	0	0	0
12	0	0	0	0	0	1	3
24	1	1	1	1	2.8	2	4
36	1	1.5	2	3	4	4.3	8
48	2.3	3	5.2	4.6	8	9.1	12.2
60	4.1	5	10.3	8.1	11.3	12.6	14.5
72	7.8	8.5	11.3	13.2	14.8	19.7	31.5

TABLE IV. EFFECT OF TREATMENT WITH 11% NaOH ON BREAKING STRENGTH OF MILDEWED COTTON DUCK

Hrs. of incubation with *Chaetomium globosum*	Strength (%)* of fabric, no further treatment	Strength (%)* of fabric, treatment with 11% NaOH
0	100	98
12	98	102
24	76	83
48	49	52
72	43	40

*Strength calculated as percentage of strength of unmildewed control fabric.

breakdown of the molecule. As stated by Pigman and Goepp [19, p. 546],

"Substances of intermediate chain length (cellodextrins) are the primary hydrolysis products, but finally oligosaccharides and glucose are obtained. . . . Mild hydrolytic conditions lead to the formation of 'hydrocellulose,' which has a diminished chain length, as is demonstrated by its low viscosity. It is sometimes defined as the material which dissolves in 8% NaOH. The decrease in chain length is also reflected in the practically complete loss of fiber strength. After additional hydrolysis, water-soluble 'cellodextrins' of high reducing power are produced."

A possible explanation for the localized character of the deterioration of the cotton fiber by *Chaetomium globosum* has been suggested by the statement of Pigman [19, p. 559] that "Native cotton cellulose and wood are much more resistant to enzymic hydrolysis than are the degraded celluloses. Since the reaction is heterogeneous in character, it is possible that one of the main variables is the surface area or relative degree of crystallinity of the substrate."

The only reference to alkali-solubility of microbiologically deteriorated cellulose found in the literature is in a paper by Bray [2]. He shows the relationship between the solubility of decayed wood pulps in 1% NaOH and their loss in weight. Furthermore, the solubility of the pulps in hot water increased as decay progressed. The loss in weight is claimed to be due to the production of gaseous material and to the solubility of the pulp in water. Also, there is a definite relationship between the alkali-solubility and the cellulose content of the pulps. In this work Bray found that little or no lignin was attacked.

Nodder [17] has developed a micromethod for measuring the extent to which a cellulosic material has been chemically modified or degraded. This method is based on the experiments of Birtwell, Clibbens, and Geake [1] on the solubility of modified cotton cellulose in caustic soda solutions. An essential part of the method is the pretreatment of the cellulosic fibers with 2% caustic soda for 6 hrs. under reflux. The object of this pretreatment is to remove noncellulosic impurities and "cellulose degradation products soluble in boiling dilute caustic soda." The actual test requires the use of 10*N* caustic soda, which is reduced to 2*N* after 15 min. This reaction occurs at 15°C, but may also be carried out at 20°C. Nodder claims that this method distinguishes between chemical damage and microbiological damage because chemical damage gives a high solubility number, whereas microbiological damage did not alter the solubility number of warp yarns which had lost 60% of their strength.

It is obvious that pretreatment of fibers with 2% caustic soda after the method of Nodder removes alkali-soluble cellulose, which may be present in localized areas and in small amounts. The unchanged solubility numbers of the microbiologically damaged fibers, as determined by Nodder, must certainly have come from the undamaged portions of the fibers. This same criticism may be directed also to the work of Searle [23] on the viscosity in cuprammonium solution of microbiologically damaged cellulose fibers. He found that there was little or no change in viscosity as compared to that of the original fibers.

3. Utilization of Glucose by Chaetomium globosum

The results obtained in Experiment 2 served as the stimulus for experiments in which the utilization of glucose by *Chaetomium globosum* was studied. The explanation given in Experiment 2 for the mode of attack of cellulolytic enzyme is similar to the classical theory of the action of "cellulase" which is given by Karrer *et al.* [14] in a paper on lichenase. It is interesting to speculate on the end-product of this enzymic breakdown. Classical theory states that glucose is the ultimate product, resulting from the breakdown of cellulose, which is required by the organisms for their growth. Prior to this work the utilization of glucose as the sole source of carbon by *Chaetomium globosum* had not been recorded. Hutchinson and Clayton [11] reported that growth of *Spirochaeta cytophaga*, a bacterium, was inhibited by reducing sugars in the presence or absence of cellulose. Such inhibition takes place even at a glucose concentration of 0.01%. Maltose was inhibitory at even lower concentrations, whereas arabinose, fructose, and galactose were inhibitory at slightly higher concentrations. These results were later confirmed by other investigators, such as Dubos [7], Winogradsky [30], and Walker and Warren [29]. It was also shown that cellobiose was inhibitive to *Spirochaeta cytophaga*, and that of all the sugars tested glucose was the most toxic.

Fahraeus [8], in reviewing this work, makes the observation that determinations of the quantities of the sugars required to inhibit growth of the organisms were never made. The statements by the various authors were based solely on observations of the

growths of organisms in tubes containing strips of filter paper and the respective sugars to be tested.

Fahraeus states that in 1941 he reported the utilization of glucose and cellobiose by *Spirochaeta cytophaga* when low concentrations of the sugars were used. When glucose and cellulose are both present in the growth medium, the cellulose is not attacked until most of the glucose has been consumed. Also, when glucose is added to a culture which is in the process of breaking down cellulose, cellulolysis ceases until the excess glucose is consumed. He concludes that "The checking of the decomposition process is more probably connected with the absence of any extracellular cellulase in the medium, which could carry on the cellulose decomposition process. When glucose enters the cells, no cellulase is required as long as sufficient amounts of glucose are available. The cellulase is perhaps not formed again until the concentration of glucose sinks below a certain level, which seems to lie at about 0.1 percent."

Fahraeus concludes by saying that although it is possible that many organisms are specialized to the extent that they will utilize only cellulose, most of the cases mentioned in the literature should be reconsidered.

Siu *et al.* [25] in a recent paper report that glucose, mannose, and cellobiose give definite growth in a qualitative experiment. The incubation period was 3 days and was carried out statically. No description of the growth was given.

In unpublished work completed before the beginning of this project it was reported that when *Chaetomium globosum* is grown on a standard liquid medium which contains cellulose as the source of carbon, glucose is found in the end-products if the growth medium is treated with glucolytic enzyme poison such as iodoacetic acid. Pringsheim [20] postulated the existence of two hydrolytic enzyme systems, cellulase and cellobiase, the former producing cellobiose from cellulose and the latter hydrolyzing the disaccharide to glucose. By the addition of antiseptics the growth of the organisms in a vigorous thermophilic fermentation was inhibited and reducing substances accumulated. These were identified as cellobiose and glucose, although the identity of the cellobiose was questionable. Similar results may be obtained by raising the incubation temperature to 40°C after the third day of incubation. Deterioration of cotton fibers appears to proceed in normal fashion.

We may postulate that *Chaetomium globosum* produces its effects on cotton by an enzyme, or enzymes (the cellulase of various authors [14, 20], secreted by the organism as soon as the spores begin to germinate). This enzyme diffuses through the growth medium, and if it fails to come in contact with cellulose, the organism ceases to grow after about 24 hrs. of germination. On the other hand, if cellulose is present the enzyme makes contact with it and cleavage begins at the 1,4 linkages. It is quite likely that the enzyme which does this is a complex enzyme system in which the action of the first enzyme serves to initiate the action of the second enzyme, and so on, until glucose is set free. The glucose, being water-soluble, readily diffuses into the mycelium and is immediately utilized by the organism for its energy requirements. In this process, presumably, phosphorylated glucolytic enzymes play their part.

Norman and Fuller [18], in discussing the subject of biological decomposition of cellulose in general, state that "It is not known whether cellulose dextrins are produced in the enzymic attack on cellulose but there seems to be some indication that two types of hydrolytic systems may be concerned, one accomplishing the primary attack, perhaps breaking cross-linkages or accomplishing substantial chain-shortening, and the other bringing about the subsequent hydrolysis of these fragments."

With regard to the statement concerning the presence of cellulose dextrins in mildewed cellulose, reference is made to Experiment 2, in which it is shown that the cellulose becomes increasingly alkali-soluble as incubation proceeds. Pigman believes [19, p. 546] this is good evidence for the presence of cellulose dextrins.

Norman [18] goes on to say that the concept of the formation of cellobiose during the breakdown of cellulose has probably come from analogy with starch. When starch is attacked by microorganisms, the disaccharide maltose is split off. Although the chain structure of starch and cellulose differ, the possibility that cellobiose is split off still exists. Norman believes that the disaccharide grouping is emphasized in cellulose by the fact that each glucose ring is turned through 180° with respect to its neighbor. Finally, Pringsheim [20] claims to have demonstrated its production by microorganisms. It should be pointed out that this work was done in 1912.

Norman considers it surprising that microorganisms should have separate extracellular enzyme sys-

TABLE V. UTILIZATION OF GLUCOSE BY *Chaetomium globosum* FOLLOWING DIRECT INOCULATION WITH SPORES

Concentration of glucose in 4-salts medium (%)	Period required for complete utilization (days)
0.01	1
0.04	2
0.09	3
0.44	6
0.90	8
2.64	14

TABLE VI. UTILIZATION OF GLUCOSE BY *Chaetomium globosum* AFTER 90% PREGERMINATION OF SPORES

Concentration of glucose in 4-salts medium (%)	Period required for complete utilization (days)
0.66	8
1.66	14
2.92	21

tems. Cellobiose is easily soluble in water, and should be able to enter the cell without hydrolysis to glucose. However, Woodman and Stewart [31] found glucose in a thermophilic cellulose fermentation that had been checked by the addition of toluene and incubated at 37°C instead of 65°C, but no cellobiose was detected. Similar results were obtained by Kalnins [13] with mesophilic cellulose organisms. On the other hand, Simola [24], working with 2 aerobic, cellulolytic bacilli, found both glucose and cellobiose in toluene-treated cultures.

Possible support for the view that the utilization of glucose is within the mycelial walls is gained from our work with extracts from *Chaetomium globosum* and *Myrothecium verrucaria*. Although these extracts do not break down native cellulose as it exists in cotton, they do break down degraded celluloses such as ball-milled cotton, cellophane, and viscose rayon. This breakdown is measured by the accumulation of glucose in the extract-cellulose mixture. Inasmuch as glucose builds up in the mixture, presumably there are no glucose-degrading enzymes present in this extract.

Inasmuch as glucose appears to be the carbon compound which is utilized within the cell walls of *Chaetomium globosum*, a medium which contains glucose should be the ideal growth mixture for the organism. However, at the Bureau of Standards and other laboratories all attempts to grow *Chaetomium globosum* on glucose-agar or glucose-broth media produced only germination of the spores and no further growth. However, incubation on a shaker in this laboratory produced excellent, although atypical, growth and utilization of glucose. The 4-salts medium previously described was used with concentrations of glucose varying from 0.01% to 2.64%. Incubation was carried on in Erlenmeyer flasks. Each flask and its contents were sterilized and when cool the specimens were inoculated with 1 ml. of *Chaetomium globosum*. The flasks were then incubated on a reciprocating shaker at 80 cycles per min. The temperature was not controlled and varied from 22°C to 28°C. Growth was evident within 24 hrs. and increased, for each concentration, up to the complete utilization of glucose. These submerged cultures showed no evidence of any but mycelial growth. This growth is unusual because macroscopically the growth substance consists of small, cream-colored globules which are from $\frac{1}{8}$ in. to $\frac{1}{4}$ in. in diameter and appear to be perfect spheres. Under microscopic examination each globule is seen to consist of a network of mycelial fibers in the center of which are approximately 10 spores or spore cases.

In order to determine whether the spores in the mycelial globules were viable or whether they were the remains of germinated spores, a quantity of mycelial globules was used as the inoculum for seeding

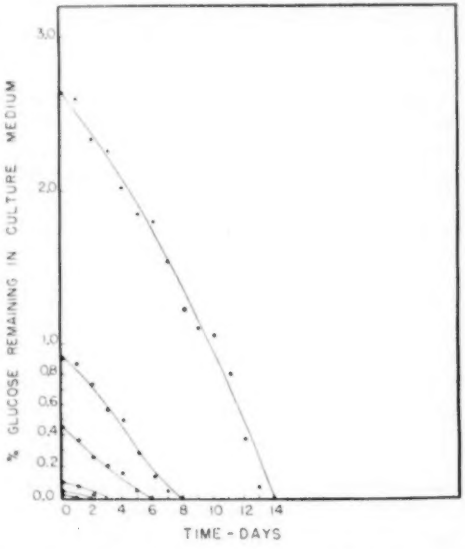

FIG. 9. *Rate of utilization of glucose by* Chaetomium globosum. *(See Table V.)*

4-salts medium containing cotton which had been ground in a Wiley mill. The cultures were incubated on a shaker at 80 cycles per min. and were examined daily for 10 days. It was found that the balls of mycelium had not grown any more and that the entrapped spores had not germinated. Microscopic examination of the cotton, by the use of alkali, revealed no evidence of microbiological deterioration.

It may be concluded, then, that these entrapped spores are not viable; however, it is of interest to note that the mycelium which normally digests cellulose has apparently lost the power to do so after growth on glucose. This observation is contrary to that of Marsh *et al.* [16]. In a recent paper these authors state that "Tests of *Chaetomium globosum*, USDA 1042.4, after twelve successive transfers on a high-sugar medium failed to indicate that this treatment had brought about any measurable loss of cellulolytic activity."

Marsh's cultures differed from ours in that they were on solid media and may have contained other carbohydrates than sugars. We have not been able to obtain growth beyond the sporulation stage when glucose is the carbon source in solid medium. Bright *et al.* [3] report that when *Chaetomium* is grown upon starch it fails to produce spores, although there is a growth of mycelium.

The utilization of glucose by *Chaetomium globosum*, as estimated by the Somogyi method [26], is given in Table V. These results are plotted in Figure 9. It is of interest to note that the curve of glucose utilization for 2.64% glucose is steeper up to the point where it reaches 0.9% residual glucose concentration than the curve of the 0.9% concentration is at its start. A similar change in slope also is observed for each of the lower concentrations as the percentage of glucose remaining is reduced and becomes equal to the next lower concentration. This shows an initial lag phase which may correspond to the period of germination.

In order to test this hypothesis the above experiment was repeated in a modified manner. Culture flasks were prepared with 4-salts medium, without glucose, and were inoculated with *Chaetomium globosum*. The flasks were shaken at 80 cycles per min. for 24 hrs., after which germination was observed to be 90% complete. At that time sterile glucose was added to each flask in order to give a range of con-

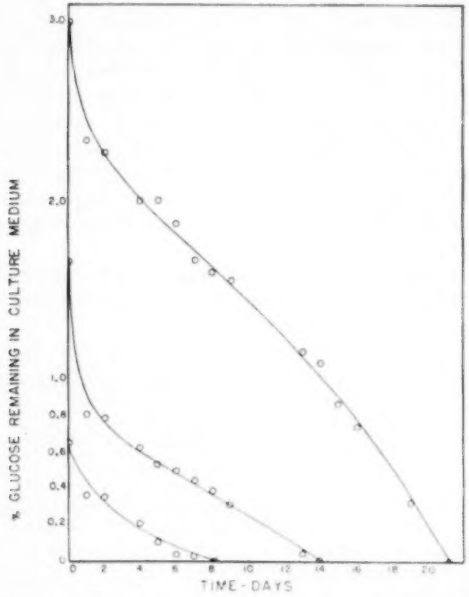

FIG. 10. *Rate of utilization of glucose by* Chaetomium globosum *after pregermination of spores.*

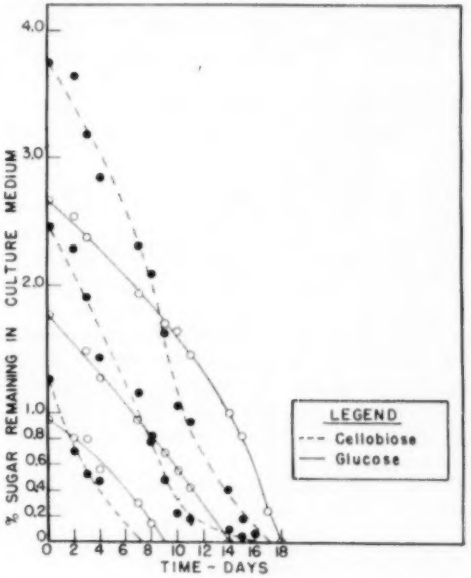

FIG. 11. *Comparison of rates of utilization of glucose and cellobiose by* Chaetomium globosum.

centrations similar to those used in the preceding experiment.

The utilization of glucose, as estimated by the Somogyi method, is given in Table VI. These results are plotted in Figure 10. It can be seen that the utilization of glucose by *Chaetomium globosum* during the first 24 hrs. is much greater for each concentration than on succeeding days. This tends to confirm the hypothesis that the lag phase in the preceding experiment corresponds to the period of germination. However, although the pregermination of the spores causes them to utilize glucose at a faster rate, the time required for complete consumption of glucose remains approximately the same.

4. Comparison of Cellobiose and Glucose as Carbon Sources for Chaetomium globosum

In pursuance of a plan to study the components of cellulose in a series of ascending complexity, cellobiose was investigated as a carbon source for *Chaetomium globosum*.

Preliminary experiments showed that growth obtained with cellobiose is similar to growth obtained with glucose. Therefore, an experiment was prepared in which a range of concentrations of cellobiose in 4-salts medium was used as the growth medium for *Chaetomium globosum*. A range of concentrations of glucose was used as a control for comparison. The inoculated specimens were incubated together on a shaker at 80 cycles per min. The incubation temperature varied from 22°C to 28°C. Residual glucose and cellobiose were estimated by the Somogyi method.

The results of this experiment are plotted in Figure 11. The curves for glucose utilization are similar to those reported in the preceding experiment (see Figure 9). However, the curves for cellobiose are steeper, and in the case of the lowest concentration (1.28%) the time of complete utilization is 7 days, as compared to 9 days for complete utilization of 0.95% glucose. The curves for the higher concentrations of cellobiose have tended to flatten off after the 10th day of incubation, which may indicate a slowing down due to the accumulation of growth products.

On the assumption that glucose is the end-product which is required by the mycelium, it seems difficult to explain why cellobiose should be utilized at a faster rate than glucose.

Although the growth product of glucose cultures has been demonstrated to be lacking in cellulolytic power, a similar experiment with cellobiose has not been performed. Such an experiment would be extremely interesting because in cellobiose we have the smallest analogue of the cellulose molecule which contains the 1,4 linkage. As Norman and Fuller [18] suggest, it is possible that cellobiose could be absorbed intact through the mycelial walls. However, if it must first be split into 2 glucose molecules, then the enzyme which breaks the 1,4 linkage may possibly be the same as the one which breaks down degraded cellulose to glucose.

5. Enzyme Studies

In order to test the hypothesis that the cellulolytic enzyme is an exoenzyme, various extracts from the growth of *Chaetomium globosum* on cellulose and on glucose have been used as substrates for various types of cellulose. An extract from *Myrothecium verrucaria*, supplied by Dr. Ralph Siu, has been used for comparison.

The test for cellulolytic activity has been adapted from Siu's work [22]. *Chaetomium globosum* was grown on Wiley-milled, dewaxed cotton for 10 days in a shake-culture. The clear yellow growth products were filtered through a fritted-glass filter and then refiltered through a Berkefeld filter. To 5 ml. of this solution in a 125-ml. flask were added 5 ml. of 0.05*M* phosphate buffer (pH 5.0) and 100 mg. of dewaxed cotton which had been pulverized in a ball mill for 24 hrs. Five drops of toluene were added to prevent the growth of microorganisms. Incubation was at 30°C for 4 days. At the end of this period the mixture was filtered, and the quantity of reducing sugar was determined by the Somogyi [26] method. Identity of the reducing sugar was determined by preparing the osazone.

In addition to ball-milled, dewaxed cotton, ground cellophane and dewaxed native cotton fibers were also used as substrates. (See Table VII.)

TABLE VII. ENZYMATIC HYDROLYSIS OF VARIOUS CELLULOSIC SUBSTRATES, USING EXTRACTS FROM *Chaetomium globosum* AND *Myrothecium verrucaria*

	Percent activity* of extract from:	
Cellulosic substrate	*Chaetomium globosum*	*Myrothecium verrucaria*
Ball-milled cotton	11.4	14.2
Ground cellophane	11.0	9.0
Native cotton	0	0

* Activity refers to the quantity of glucose formed in 4 days, expressed as percent of the cellulosic substrate.

The *Chaetomium globosum* extract was not concentrated before use and therefore represents a very crude extract. The *Myrothecium verrucaria* extract was marked as being 12% active. In a letter, Dr. Siu indicates that this is not a very active preparation "but is about average."

In a paper entitled "A Cellulolytic Enzyme Preparation from *Myrothecium verrucaria*," Saunders, Siu, and Genest [22] state:

"Cellulolytic enzyme preparations active against various forms of cellulose have been reported by a number of investigators who have used a variety of different sources. Fungi which have been employed for the preparation of such extracts are *Sporotrichum carnis*, *Aspergillus oryzae*, *Merulius lachrymans*, and *Coniophora cerebella*, and bacteria used have included *Bacterium protozoides*, *Bacterium bosporum*, *Cellulobacillus myxogenes*, *Cellulobacillus mucosus*, *Plectridium cellulolyticum*, several species of *Cytophaga*, and various thermophilic, cellulose-decomposing bacteria. In addition, active cellulolytic extracts have been prepared from the intestinal juice of the snail *Helix pomatia*, from green malt, and from the protozoan *Eudiplodinium neglectum*, which was isolated from cattle rumen. Although the data presented by several of these investigators are certainly suggestive of true cellulolytic enzyme activity, nevertheless these workers in general have not conclusively established the cell-free nature of their preparations. This is of considerable importance in view of the failure of other investigators to obtain cell-free cellulolytic enzymatic preparations from fungi. Questions were raised as to the possibility of bacterial or fungal contamination during the period (usually several days or more) of testing for cellulolytic activity."

The paper quoted above describes the preparation and some properties of a cell-free cellulolytic enzyme from *Myrothecium verrucaria*. The object of the present experiment was to carry out similar studies with extracts of *Chaetomium globosum*.

From the results it appears that the unconcentrated *Chaetomium globosum* extract is about as active as the *Myrothecium verrucaria* extract. Neither of the extracts is capable of causing breakdown of native cotton fibers, as measured by glucose formation. However, the possibility that a localized attack is made on some of the fibers should be investigated by studying the reaction of these fibers to caustic soda. If localized attack does take place, the quantity of glucose which would be elaborated might be too small for even the Somogyi test to detect.

As mentioned previously, a yellow extract was obtained from the growth of *Chaetomium globosum* on glucose. This extract has been tested for cellulolytic activity with ball-milled cotton, ground cellophane, and dewaxed native cotton fibers. There was no evidence of cellulose breakdown, as measured by increase in reducing sugar.

This latter experiment should be repeated with cellobiose as the carbon source. It would be interesting to learn whether or not the presence of a 1,4 linkage stimulates the secretion of cellulolytic enzymes.

6. Infrared Studies

In order to make use of the newer techniques of analysis in the study of the mechanism of cellulolysis, infrared analysis was carried out in collaboration with Dr. John W. Rowen [21] at the National Bureau of Standards. Since his apparatus requires the use of thin films, and because he had already obtained data on the infrared transmission of regenerated cellulose films, these were used as substrates for *Chaetomium globosum* and for cellulolytic enzymes.

Inasmuch as infrared spectroscopy has shown the presence of individual groups in a molecule—such as CO, OH, COOH groups, and others—it was felt that this method of analysis might give a clue as to the mechanism of deterioration. Because of difficulties encountered in the study of the end-products of *Chaetomium globosum*, it was felt that if the organism changes the structure of the cellulose upon which it feeds, the transmission characteristics of the cellulose might be changed.

A film of regenerated cellulose was divided in half, one half being used as a control. The other half was used as a substrate for *Chaetomium globosum*. After 12 hrs. of incubation at 28°C the film was carefully removed from the agar plate, washed free of growth, and dried. Incidentally, specimens of regenerated film which were incubated for longer than 12 hrs. were too badly deteriorated to be harvested in one piece.

The results show that the characteristic absorption bands of cellulose appear in both the mildewed specimen and the control, except that the percentage transmission of the mildewed film is greater than that of the control, with several exceptions in the region of from 4 μ to 5 μ and from 10.4 μ to 12.2 μ.

The above experiment was repeated with thicker films to determine whether the exceptions were reproducible. In this experiment additional films were used. Two specimens were incubated with *Chaetomium globosum*. One was washed after incubation, and the other was immediately dried without wash-

ing. Also, a specimen was treated with *Myrothecium verrucaria* extract for 4 days.

The results show that the difference in transmission appears to result from the loss in thickness of the films. It is interesting to note that the enzyme-treated specimen had the highest percent transmission. The exceptions noted in the first experiment were not reproduced in this experiment.

These results are quite in line with what we already know. If the organisms during their growth create soluble products from the cellulose, then they leave nothing but unreacted cellulose.

7. Cellulose and Sugar Derivatives as Carbon Sources for Chaetomium globosum

Cellulose acetate has previously been known to be resistant to cellulolytic molds [6, 9, 27, 28]. Because of our success in growing *Chaetomium globosum* on a glucose substrate in shake-culture, it was decided to study cellulose acetate as a substrate for *Chaetomium globosum* in shake-culture. For this experiment cellulose acetate flake and partially acetylated cotton were used. They were prepared by grinding in a Wiley mill and also by pulverizing in a ball mill for 24 hrs.

These materials, together with Wiley-milled cotton as a control, were incubated with *Chaetomium globosum* in 4-salts medium on a reciprocating shaker at 80 cycles per min. After 10 days of incubation no growth was observed on the cellulose acetate or partially acetylated cotton cultures, although excellent growth was obtained on the cotton controls.

If the resistance to cellulolysis of cellulose acetate is based on its "crystallinity," it is difficult to understand why ball-milled cellulose acetate and especially ball-milled partially acetylated cotton should be so resistant to mold growth. On the other hand, if resistance is due to acetylation, it is difficult to explain the resistance of partially acetylated cellulose on the same basis as that of fully acetylated cellulose.

The preceding experiment has led to the study of acetylated analogues of cellulose.

Because cellobiose octacetate was available, as the result of preparation in our laboratory by a student, it was studied first. Surprisingly, this compound gave as good growth of *Chaetomium globosum* in shake-culture as did cellobiose, which was used as a control. Repeating this work, 20 g. of cellobiose octacetate were prepared, and 10 shake-cultures were prepared, with cellobiose cultures as controls. In making up concentrations of cellobiose octacetate it was found that the solubility of the compound was so low that it was pointless to prepare a graded series of concentrations as in the case of glucose or cellobiose. Therefore, all 10 of the samples were made up to 1% concentration by weight. Again, excellent growth of *Chaetomium globosum* was noted. Growth was permitted to go on for 3 wks., during which time it was noted that the quantity of undissolved cellobiose octacetate decreased, until at the end of 3 wks. practically no undissolved material, except for the mycelium of *Chaetomium globosum*, was present in the flasks.

Finally, a sample of cellobiose octacetate from Eastman Kodak was tested in the same manner as in the preceding experiment, and similar growth was noted.

The above experiments have been repeated with glucose pentacetate, obtained from Eastman Kodak, with glucose as a control. Again, growth of *Chaetomium globosum* was noted. As growth proceeded, the undissolved glucose pentacetate went into solution. The fact that in the case of glucose pentacetate and cellobiose octacetate the undissolved portion dissolved as growth took place indicates that even though there may have been impurities present the organism must have derived most of its nourishment from the sugar acetates.

It is interesting to consider the possible mechanisms by which *Chaetomium globosum* utilizes the 2 sugar acetates. The fact that these compounds are relatively insoluble should not be considered to preclude the possibility that *Chaetomium globosum* does grow upon them. It should not be forgotten that cellulose itself is even more insoluble than the sugar acetates.

If we assume that the organisms first hydrolyze off the acetyl groups and then utilize the liberated glucose or cellobiose, as the case may be, then it becomes difficult to explain why they fail to do so in the case of cellulose acetate and of partially acetylated cotton.

From this work it appears that acetylation does not confer mildew-resistant properties upon cellulose degradation products. On the other hand, if ball-milling can be said to alter the "crystallinity" of cellulose acetate and if, as we have shown, ball-milled cellulose acetate resists *Chaetomium globosum*, it must be admitted that we have not yet determined the mechanism by which cellulose acetate resists cellulolytic enzymes.

TABLE VIII. CARBOHYDRATES AND VARIOUS OTHER MATERIALS APPARENTLY UTILIZABLE BY *Chaetomium globosum* SHAKE-CULTURES

Substrate*	Growth of *Chaetomium globosum*
l-Arabinose	Heavy growth of mycelial balls
d-Xylose	Very heavy mycelial growth in the form of a gelatinous mat
l-Rhamnose	Moderate fibrous growth
d-Fructose	Heavy growth of mycelial balls
d-Galactose	Heavy growth of mycelial balls
d-Mannose	Heavy growth of mycelial felt and few very large mycelial balls
Maltose	Very heavy growth of mycelial balls
Sucrose	Heavy growth of mycelial balls
d-Lactose	Heavy growth of mycelial balls and fragments
Raffinose	Moderate growth of mycelial balls and mycelial felt
Gluconic acid	Heavy growth of mycelial mat
Pyruvic acid	No growth
Acetic acid	Moderate growth of mycelial mat
Oxidized cellulose (polyglucuronic acid)	Sometimes a heavy growth of mycelial mat
Inositol	Heavy growth of mycelial mat
Castor oil (not a carbohydrate)	Very heavy growth of mycelial mat

* 0.5 g. in 50 ml. of 4-salts medium, except with castor oil.

It was after completion of these experiments that the recent paper by Siu *et al.* [25] came to our attention. In this paper is reported the fact that cellobiose octacetate and glucose pentacetate do not support the growth of various molds, including *Chaetomium globosum*. Communication with Dr. Ralph Siu has elucidated the fact that these cultures were incubated statically, which may account for the difference in results. However, Siu *et al.* report that under the same conditions glucose, mannose, and cellobiose do support a definite growth, although no indication is given as to the method of observation or the nature of the growth substance.

8. Other Sugars and Carbohydrates as Carbon Sources for Chaetomium globosum

Because it has been possible to grow *Chaetomium globosum* on substrates other than cellulose by using shake-cultures, the possibility of growing this organism on other sugars and carbohydrates was investigated.

Fahraeus [8], in a review of the influence of soluble carbohydrates on cellulose decomposition, concludes that most authors found reducing sugars to be inhibitive to the growth of the various organisms which were used, and that they have thus assumed that cellulose is the only utilizable source of carbon.

Fahraeus studied various sugars as carbon sources both in the presence and in the absence of cellulose. He found that when glucose was present in the medium with cellulose it was used preferentially, and cellulose was not broken down appreciably until practically all of the glucose was exhausted. This was also true when cellobiose and mannose replaced glucose. He states: "Regarding other sugars it seems, however, probable that they are not able to support growth of *Cytophaga*. In any case, the sugars in question are not greatly preferred to cellulose."

As stated previously, Siu *et al.* [25] obtained growth in static culture with glucose, mannose, cellobiose, and methyl-β-*D*-glucoside.

The object of this experiment was to determine whether *Chaetomium globosum* can grow on carbon sources other than cellulose, glucose, and cellobiose. If the organism can be made to grow on a large number of substances having some common configuration, additional knowledge of the mode of action of cellulolysis may be gained. On the other hand, it should be understood that organisms are capable of secreting a variety of enzymes, depending upon the composition of the substrate. Therefore, wherever growth is noted the possibility must be considered that noncellulolytic enzymes are used to digest noncellulosic substrates. (See Table VIII.)

It is obvious that much work remains to be done in this field. However, a start has been made by showing that *Chaetomium globosum* will digest a variety of sugars, carbohydrates, and even the fatty acids of castor oil.

Summary

The results obtained in these experiments include:

1. Determination was made of loss of tensile strength of cotton duck during the first 72 hrs. of incubation using 5 cellulolytic organisms—*Thielavia* sp., *Humicola* sp., *Stemphylium* sp., *Chaetomium globosum*, and *Myrothecium verrucaria*.

2. A study of mildewed fibers in dilute alkali, suggested by Clegg's Congo red test [4], has shown the localized nature of attack by cellulolytic molds and the production of alkali-soluble material in the areas. As the attack proceeds, the cellulose becomes soluble in decreasing concentrations of alkali and finally becomes soluble in water.

3. In an attempt to identify the material in the alkali-soluble regions by infrared absorption, changes

in cellulose films after partial digestion by *Chaetomium globosum* were studied by infrared absorption in cooperation with Dr. John W. Rowen at the National Bureau of Standards. No significant effects were found other than reduction in thickness of the films.

4. The following indirect methods for the identification of cellulose decomposition products were used:

(*a*) Study of the action of cellulolytic molds on sugars and sugar derivatives. *Chaetomium globosum* is capable of utilizing a wide variety of sugars, especially in shake-cultures.

(*b*) Testing of cellulose derivatives such as cellulose acetate, partially acetylated cellulose, cellobiose octacetate, and glucose pentacetate. Although no growth is obtained with cellulose acetate or partially acetylated cellulose, even when the fibers are ball-milled, excellent growth of *Chaetomium globosum* is obtained with cellobiose octacetate and glucose pentacetate in shake-cultures.

5. Enzyme extracts from *Chaetomium globosum*, obtained in this laboratory, digest degraded forms of cellulose but not native cotton fibers. These results are similar to results with *Myrothecium verrucaria* obtained by Dr. R. G. H. Siu, of the Philadelphia Quartermaster Laboratories.

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The Relaxation of Stress in Wool Fibers

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Contribution of The Textile Foundation and Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Abstract

A study of the decay of tension of Columbia 56's wool fibers maintained at constant temperature and extension has been carried out in water, in solutions of sodium bisulfite of various concentrations, and in neutral salt solutions.

The experimental results obtained in water are similar although not identical to the results previously found by Speakman and Shah for human hair. The rapid stress decay of stretched wool which occurs when sodium bisulfite is added appears to be due to a chemical reaction involving the cystine linkages. The rate becomes independent of bisulfite concentration at sufficiently high concentrations. A much slower but unexpectedly large stress decay occurs in the presence of neutral salts such as sodium chloride.

Introduction

Under certain conditions, the process of stress relaxation in cross-linked elastic systems has been attributed to the breaking of primary bonds followed by molecular rearrangement. In hydrocarbon rubbers, stress relaxation at high temperatures has been related to the oxidative scission of the bonds making up the three-dimensional network [5, 6]; whereas polysulfide rubbers have been shown to relax as a result of a metathetic process which involves disulfide linkages and sulfhydryl or other groups [1, 4].

In keratin fibers, the breakdown of cross-linkages between the polypeptide chains followed by molecular rearrangement has been proposed to account for stress relaxation [3]. The cross-bonds present in keratin fibers include linkages due to van der Waals' forces, hydrogen bonds, electrostatic salt bonds, and, most important, the covalent disulfide linkages of the cystine units.

The process of stress decay at constant extension is accelerated by increased relative humidity, fiber extension, and temperature, as Speakman and his coworkers have shown [2, 3]. These same authors observed that pretreatment of the fiber with chemical reagents which cause breakdown of the disulfide bond will increase the rate of the relaxation process, while those reagents which stabilize the disulfide bond or cause reduced swelling in water will decrease the relaxation rate.

Although chemical pretreatment will cause a change in the relaxation rate, the resultant process is a complex combination of the normal relaxation which occurs whenever the fiber is elongated and the additional effects due to the chemical attack. It was thought that the effect of the chemical reagent could be better isolated by elongating the wool fiber in water and allowing it to relax until the rate becomes relatively slow on a linear time plot, at which time the reagent could be added and the kinetics of the reaction could be studied by the additional relaxation produced.*

In this paper, the results of a study of the relaxation of wool produced by sodium bisulfite and neutral salt solutions are presented. In addition, the normal relaxation in water as a function of temperature and elongation and the effect of pretreatment with sodium bisulfite solutions are considered.

Description of Apparatus and Experimental Procedure

The apparatus used for this series of experiments was a modified form of the relaxation balance used by Tobolsky, Prettyman, and Dillon [6] for the study of rubber. A photograph of the relaxometer is shown in Figure 1 and a schematic diagram in Figure 2.

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* Shortly before the completion of the work described in this paper, it was learned that Dr. Harold Lundgren, of the Western Regional Research Laboratory, had developed an essentially identical procedure.

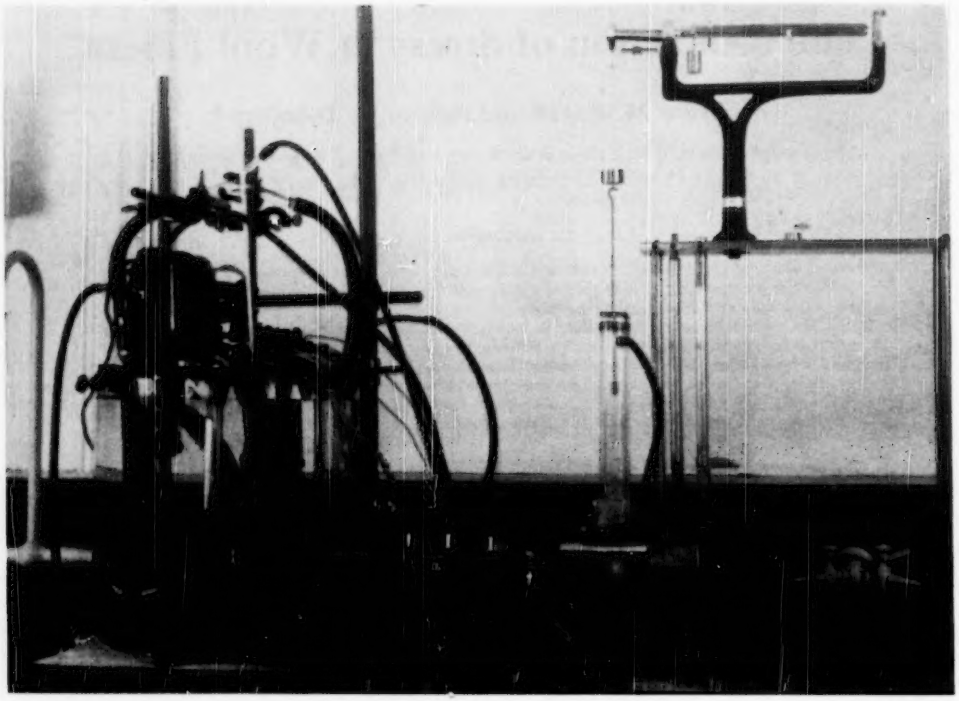

FIG. 1. *Photograph of relaxometer and temperature bath.*

The tension of the elongated fiber was measured by a Sargent triple-beam balance, S-3435. This balance has a sensitivity of less than 10 mg., which is sufficient for the present purposes, is very stable to shocks, and damps out its oscillations rapidly. The ratio of beam lengths is about 3.5 to 1, and by placing stops on the end of the long arm the fiber length was maintained constant to within 0.56 mm.

The fiber was mounted in two small clamps, each made of two brass strips which were held tightly together by two small screws. The upper clamp was soldered to a length of $\frac{1}{8}$-in. stainless steel wire with a hook at the other end for attachment to the balance, while the lower clamp was attached to a lead cylinder which was machined to fit snugly into a double-jacketed glass tube. The lead cylinder weighed 100 g., which was much more than the maximum tension encountered in the experiments, thus insuring that the weight was never lifted from the bottom of the tube by the fiber tension. The clamps, lead weight, and steel wire were silver-plated to minimize corrosion by the various solutions used.

The jacketed tube was cemented into a Plexiglas block rigidly fastened into a Textolite base which in turn was attached to a movable platform. Elongation of the fiber was controlled by a threaded column, which, when rotated, raised or lowered the platform. The motion of the platform was measured by means of vernier calipers. The scale of the calipers was mounted on the base of the relaxometer and perpendicular to it—that is, in the direction of motion of the platform—while the vernier was securely attached to the movable platform and moved with it.

Temperature control was attained by circulating water from a constant-temperature bath through the outer jacket of the glass tube. The temperature in the inner cylinder was determined by means of an Anschütz thermometer which was suspended inside. This thermometer was graduated in intervals of 0.2°C and could be read to 0.1° by the use of a

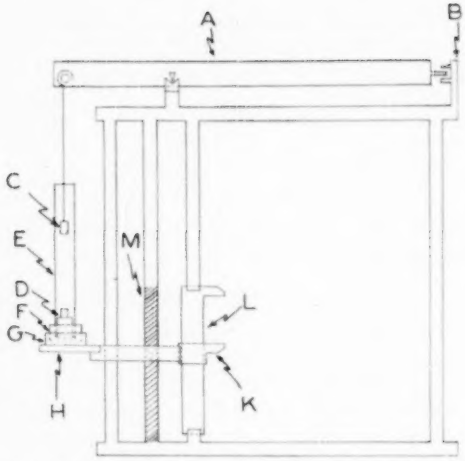

FIG. 2. *Schematic diagram of relaxometer.* A—*Balance beam.* B—*Beam motion stops.* C—*Upper fiber clamp.* D—*Lower fiber clamp and weight.* E—*Double-jacketed glass tube.* F—*Plexiglas block.* G—*Textolite base.* H—*Movable platform.* K, L—*Vernier calipers.* M—*Threaded column.*

magnifying glass. During the course of an experiment, the temperature was found to remain constant within this limit of $\pm 0.1°$.

In order to minimize the errors involved in measuring the length of the fibers and maintaining constant length during the course of an experiment, fibers of 90-mm. length or longer were used. All tension measurements were corrected for the buoyancy of the steel wire attached to the upper clamp.

During the time when the rate of relaxation was very rapid, tension readings were taken by setting the balance at a value below the fiber tension and noting the time at which the beam went through the balance point. After the rate of relaxation had become slower, readings were taken by bringing the beam to balance at definite time intervals.

Before extension, the fibers were soaked in water overnight to allow the regain to approach equilibrium.

The work in this paper was all carried out on Columbia wool, 56's grade, cleaned by extraction in ether, followed by washing in running water.

Experimental Results and Discussion

A microscopic examination of several of the Columbia wool fibers showed a great degree of nonuniformity in the individual fibers. In some cases the diameter of a single fiber varied by as much as 100% along the length of the fiber. In view of this nonuniformity, the following results are given in terms of tension, the total retractive force exerted by the fiber, rather than in terms of stress, the force per unit cross-sectional area.

With such a large intra-fiber variability, it is not surprising to find a large inter-fiber variability as well. Two apparently identical fibers taken from the same staple and elongated under seemingly identical conditions to the same extension very often had widely different tensions at equivalent times. Even in the case of Cotswold wool, which is noted for its uniformity, a large variability in the relaxation behavior of different fibers has been observed [2]. In this latter case, the rate of relaxation was measured by the half-tension time. For the present purposes, the half-tension time was not used as a measure of

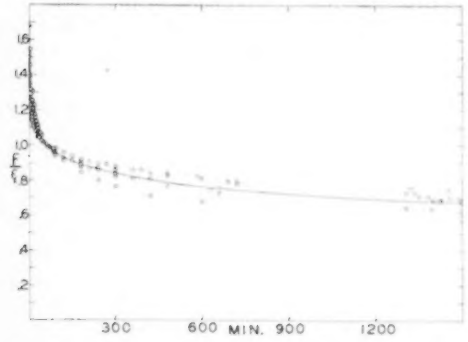

FIG. 3A. *Relaxation of 10 different fibers in water at 15% extension and 50°C. Linear time scale.*

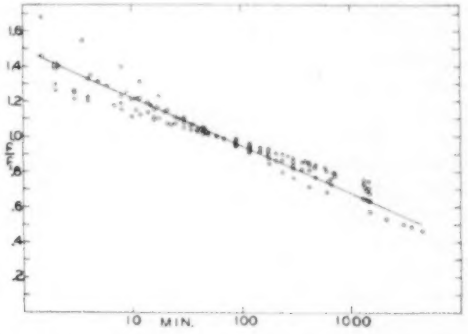

FIG. 3B. *Relaxation of 10 different fibers in water at 15% extension and 50°C. Logarithmic time scale.*

TABLE I. RELAXATION IN WATER

Temperature (°C)	Elongation (%)	No. of fibers studied	Range of f_1 values (g.)
30	5	5	1.39–1.95
30	15	4	1.99–3.41
30	25	2	2.40–4.20
50	5	1	3.49
50	15	10	1.47–3.35
50	25	2	2.47–3.61
70	15	3	0.75–1.07
80	15	3	0.62–1.10

relaxation, since it would have required excessively long time periods to determine this quantity at the lower temperatures. It was found, however, that the use of relative tension, f/f_a, where f_a is the tension of the fiber at some reference time t_a, gave a good degree of fiber-to-fiber reproducibility. Some indication of the reproducibility attained by the method is shown in Figure 3 (A and B), in which the relaxation in water at 50°C and 15% extension of 10 different fibers is presented in a plot of f/f_1 versus linear and logarithmic time, respectively, where f_1 is the tension 1 hr. after stretching. In Figure 3, a great many of the experimental points for different fibers lie so close together that it is impossible to show them all. The points which are shown are representative of the maximum deviations obtained from experiment to experiment.

Relaxation in Water

The relaxation of Columbia wool when elongated in water was studied as a function of temperature and percentage elongation. In Table I are listed the temperature and elongation for each set of experiments, the number of fibers studied under each set of conditions, and the range of f_1 values observed.

Qualitatively, the relaxation behavior of Columbia wool is similar to that observed by Speakman and his coworkers [2, 3] for Cotswold wool and human hair. When plotted against logarithmic time, the relaxation curve is slightly concave to the time axis at 30°C, practically a straight line at 50°C, and convex to the time axis at 70°C and 80°C. At the higher temperatures, however, the initial portions of the curves are almost linear, and the departure from linearity at later times may be caused by the fact that relaxation at these temperatures is so rapid that the tension approaches an asymptotic value in a relatively short time.

TABLE II. INITIAL RELAXATION IN WATER (VALUES OF k IN EQUATION $f/f_1 = A - k \ln t$)

Temperature (°C)	Percentage elongation: 5%	15%	25%
30	0.029	0.063	0.071
50	0.072	0.106	0.106
70		0.334	
80		0.411	

If this is so, then the initial relaxation of the fibers may be approximately fitted by the equation

$$f/f_1 = A - k \ln t, \qquad (1)$$

and the values of k will indicate the effect of temperature and elongation on the relaxation rate.

In Table II the average values of k for each set of conditions are given. From this tabulation we may conclude that an increase in the temperature will cause an increased relaxation rate, but that the magnitude of this increase diminishes as the extension is increased. Similarly, an increase in the extension will cause an increased rate of relaxation, but to a lesser extent at higher extensions and temperatures.

Although the measurement of the slopes enables a quantitative determination of the effect of temperature and extension on the relaxation rate, the results apply only to the initial stage of the process. A qualitative comparison of the over-all process is furnished by plotting on one figure the average relaxation results for different temperatures at one extension or for different extensions at one temperature. One such plot is shown in Figure 4, where the averaged relaxation results at 15% elongation and 30°C, 50°C, 70°C, and 80°C are plotted. This plot indicates the same general effect of temperature and extension which is shown in Table II.

It has been shown that plotting relaxation results in terms of relative tension indicates a good degree of fiber-to-fiber reproducibility. Nevertheless, as Figure 3 shows, the results do exhibit a significant scatter. This scatter, which is probably caused by sample variance, is large enough to mask any small-magnitude effects. The data for the 10 fibers plotted in Figure 3, for example, gave k values which varied from 0.076 to 0.192, with an average value of 0.106. As a rough estimate, therefore, it appears that a change in k by a factor of 3 or more can be considered significant; any change of lesser magnitude may be caused by the sample variance. The above results when compared with those of Speakman and Shah [3] indicate that Columbia wool is somewhat

TABLE III. PRETREATMENT OF COLUMBIA WOOL FIBERS WITH 0.1*M* SODIUM BISULFITE SOLUTIONS (50°C, 15% EXTENSION)

Treatment No.	Treatment	Repetitions	Range of f_1 values (g.)
I	In bilsulfite for 17 hrs. Washed out thoroughly 1 hr. before stretching. Stretched and relaxed in water.	1	0.93
II	In bisulfite for 20–21 hrs. Stretched and relaxed in bisulfite.	2	0.31–0.52
III	In bisulfite 5 min. before stretching. Stretched and relaxed in bisulfite.	2	0.36
IV	Bisulfite added to fiber at time of stretching. Relaxed in bisulfite.	1	0.23

different from human hair in relaxation properties, although many points of similarity do exist.

Relaxation in Sodium Bisulfite Solutions

In this portion of the work, the wool fibers were immersed in 0.1*M* sodium bisulfite solutions for varying time intervals before stretching, as shown in Table III. All of these experiments were performed at 50°C and 15% extension. The results (averaged where repetitive experiments were performed) are shown in Figure 5 in comparison with the average behavior for untreated fibers in water under the same conditions (Curve O).

It is important to bear in mind that the fiber property under consideration here is the rate of relaxation and nothing else. No attempt is made to determine whether bisulfite treatment softens or stiffens the fiber. In Table III is listed the range of f_1 values for each treatment. Comparing these values with the observed range of 1.47 to 3.35 g. for untreated fibers would suggest a softening action. At the present time, however, we are unable to compare absolute tensions and must leave the matter for further investigation.

When the fiber is left standing in the bisulfite solution during relaxation (Treatments II, III, and IV—see Table III), the rate of relaxation is greater than for untreated fibers, as Speakman and Shah [3] have shown, and increases as the period of pretreatment decreases.

On the other hand, if the bisulfite is thoroughly rinsed out of the fiber before extension in water (Treatment I—Table III), the fiber relaxes at a rate which is practically the same as that of the untreated fiber.

Since relaxation occurs in wool without the addition of bisulfite, the isolated effect of this reagent can best be studied only after it has been separated from the other relaxation processes. Consequently, experiments were carried out by adding the bisulfite solutions to the stretched fiber 20 to 25 hrs. after it had been extended in water. Although the fiber is still undergoing relaxation in water after 20 hrs. or more, the rate at which it is occurring is relatively so slow that it may be neglected in comparison with the rapid relaxation caused by the addition of bisulfite.

The results of these experiments at 30°C and 50°C indicate that for bisulfite concentrations of 0.05*M*,

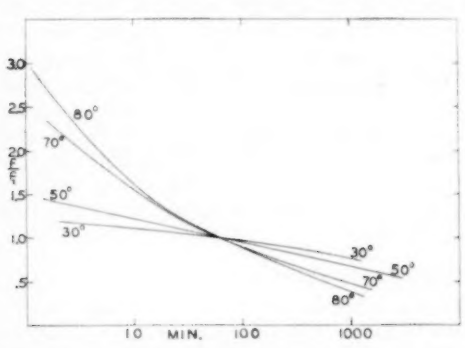

FIG. 4. *Average relaxation in water at 15% extension as a function of temperature.*

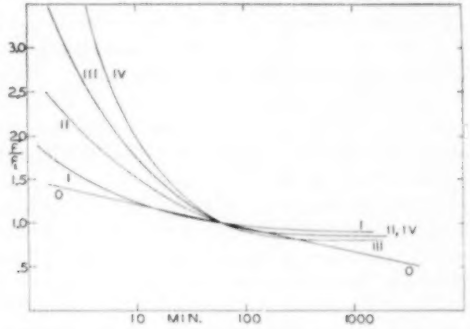

FIG. 5. *The effect of pretreatment with 0.1M sodium bisulfite at 15% extension and 50°C. (See Table III for key to the Roman numerals.)*

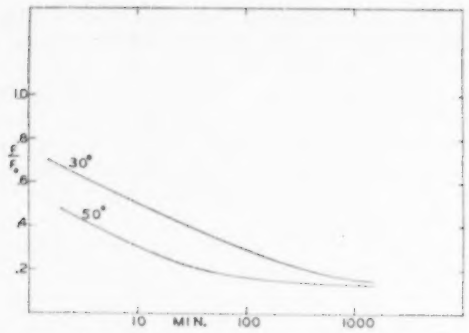

FIG. 6. *The effect of the addition of sodium bisulfite to extended fibers previously relaxed in water.*

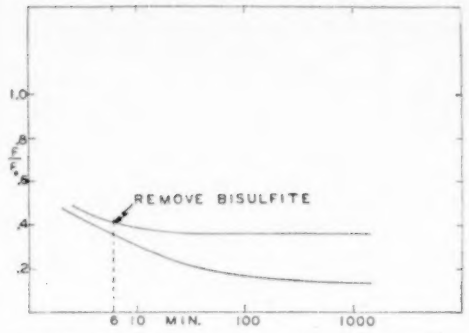

FIG. 7. *The effect of the addition of 0.1M sodium bisulfite to an extended and relaxed fiber, followed by its removal after 6 min., compared with the relaxation occurring when the bisulfite is not removed.*

0.1*M*, and 1.0*M*, and for fiber extensions of 5%, 10%, 15%, and 25%, the rate of relaxation is independent of the concentration of the reagent and the elongation of the fiber, within the experimental error. Some minor effects may be present, but they are completely masked by the spread of results from fiber to fiber.

Although the experimental error causes some overlap of the results at the two temperatures, there is a definite increase in the relaxation rate caused by a temperature increase of 20°C, as shown in Figure 6. In this figure are plotted the average relaxation results for the two temperatures—10 experiments at 30°C and 8 at 50°C, in each case covering the range of concentrations and extensions given above. The results are plotted in terms of f/f_0 against logarithmic time, where f_0 is the tension attained by the fiber in water at the moment the bisulfite is added, and this time is taken as zero time.

The complete mechanism of relaxation involves not only the chemical breakdown of the cystine bonds, but also the subsequent molecular rearrangement. Only if the rate-determining step in this process is the breaking of bonds, or some preceding step, can the rate of relaxation be related to the kinetics of the reaction of sodium bisulfite on wool.

In order to study this phase of the problem, an experiment was carried out in which the fiber, after 24 hrs. relaxation in water at 15% extension and 50°C, was allowed to react with 0.1*M* sodium bisulfite for only 6 min. and then the bisulfite was thoroughly rinsed out while the fiber remained stretched. The results are shown in Figure 7 in comparison with the 50°C curve replotted from Figure 6. It is apparent that relaxation stops shortly after removal of the bisulfite and that the relative tension levels off at a much higher value.

In addition to the above experiments with high concentrations of bisulfite, several experiments using extremely dilute concentrations of bisulfite at 15% extension and 30°C were performed. In the experiments with concentrated solutions, small concentration changes caused by reaction with the fiber or by air oxidation were shown to have a negligible effect. In dilute solutions, however, the effect of concentration changes is more marked; therefore, during the course of these experiments with dilute concentrations the bisulfite was replaced at intervals by fresh solutions—in the early part of the relaxation the solutions were replaced half-hourly, and at longer intervals later on. The concentrations studied were $1.5 \times 10^{-3}N$, $1.8 \times 10^{-4}N$, and $4.5 \times 10^{-5}N$ and the results are shown in Figure 8. It can be seen from the figure that the use of very dilute solutions of bisulfite slows down the relaxation process considerably. The curves in Figure 8 for low concentrations resemble somewhat the e^{-kt} curves reported for rubbers [1, 4, 5, 6] but this expression does not fit the wool data exactly. The decay curve for the highest concentrations deviates even more from the e^{-kt} law.

Relaxation in Neutral Salt Solutions

When concentrated solutions of sodium bisulfite were added to the stretched wool fibers, the first measurements recorded indicated a 25% or greater decrease in the tension. It is of interest to ascer-

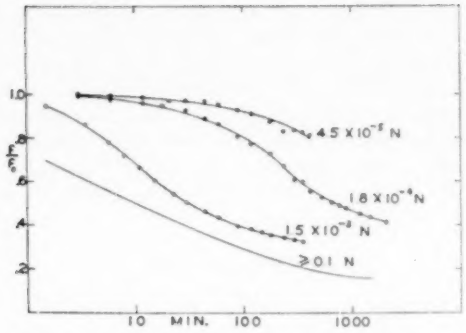

FIG. 8. *Relaxation caused by the addition of low-concentration bisulfite solutions to extended and relaxed fibers, compared with high concentration results, at 15% extension and 30°C.*

tain whether or not this immediate decrease was a simple thermodynamic effect due to the changed thermodynamic potential of the water in the liquid phase. Experiments with neutral salt solutions show that only slight immediate changes in relative tension occurred by way of this mechanism. These experiments also revealed, surprisingly, that a slow relaxation of tension occurred in the presence of these neutral salt solutions, as shown in Figure 9. In this figure is plotted the relaxation of a fiber in a 1.0*M* sodium chloride solution at 15% extension and 50°C following 25 hrs. relaxation in water, with zero time taken as the time of addition of the salt solution.

In order to compare the magnitude of this neutral salt effect with the previous relaxation in water, we

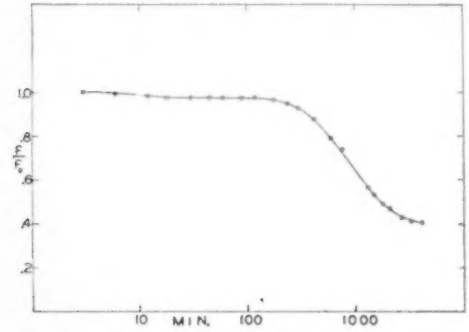

FIG. 9. *Relaxation of fiber following the addition of 1.0*M *sodium chloride after 25 hrs. relaxation in water, at 15% extension and 50°C. Zero time is the time of addition of the salt.*

have replotted the above data in Figure 10. In this figure, zero time is the time at which the fiber was first extended, and it can be seen that the addition of sodium chloride causes a definite discontinuity in the complete relaxation curve.

Further experiments appear to indicate that the effect of the neutral salt is independent of temperature in the range 30°C to 70°C and relatively independent of salt concentration in the range 0.1*M* to 1.0*M*.

The nature of the reaction occurring between the wool and the salt is somewhat obscure. The relaxation behavior indicates that two processes are taking place. One process occurs rapidly and accounts for only a minor decrease in tension, whereas the other process is comparatively slow, is responsible for a large stress decay, and can be fitted very closely by an e^{-kt} curve.

Summary

A study of the decay of tension of Columbia 56's wool fibers maintained at constant temperature and extension has been carried out in water, in solutions of sodium bisulfite of various concentrations, and in neutral salt solutions.

A direct comparison of the results for different fibers is not possible because of the large sample variance encountered. The use of relative tension, however, enables a comparison, although the sample variance is still sufficient to conceal any effects of small magnitude.

When extended and allowed to relax in water, Columbia wool undergoes stress relaxation somewhat similar to that reported for human hair. The relaxa-

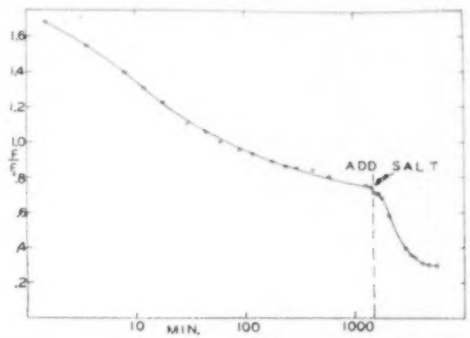

FIG. 10. *A replot of Fig. 9 with zero time taken as the time at which the fiber was extended.*

tion process is approximated by an equation linear in logarithmic time, and, as for human hair, the rate of the process is increased by increase in temperature or fiber extension. The magnitudes of the temperature and extension effects, however, are such as to suggest major differences in the properties of Columbia wool and human hair.

The addition of solutions of sodium bisulfite to wool changes the properties of the material by a chemical process and this change is made evident by the relaxation behavior. When the bisulfite is added before extension of the fiber, the rate of relaxation after extension is increased, provided the fiber is left in the bisulfite. This increase in the relaxation rate becomes greater as the period of treatment decreases. If the bisulfite is thoroughly rinsed out with water before extension, the relaxation rate is practically identical with that of the untreated fiber.

The relaxation occurring when bisulfite solutions are added to fibers which had been previously extended and relaxed in water was also studied. The rate of stress relaxation in these cases depends on concentration at low bisulfite concentrations but becomes independent of the concentration above 0.05*M*. An increase in the temperature will speed up the reaction, while extension is apparently without effect.

Solutions of neutral salts will cause extended and relaxed fibers to undergo an additional relaxation. Under these conditions, there occurs a small but rapid decrease of stress followed by a slow stress decay of large magnitude.

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Wool Research

AN analysis of some of the principal areas in which research can benefit the woolen and worsted industry is contained in a booklet issued by The Wool Bureau. The report, which is based on an eight-month survey of research centers and wool textile mills in this country by Giles E. Hopkins, Technical Director of The Wool Bureau, is worthy of study by the textile and chemical industries.

In addition to specific recommendations as to the direction of attack on the problems of production, marketing, manufacture, and service, the report estimates the practical significance of each. An appendix outlines the studies which are at present in progress in this country.

This report, titled "Suggested Research and Development Studies for the Woolen and Worsted Industry," may be obtained by writing to The Wool Bureau, Inc., 16 West 46th St., New York 19, New York.

Stabilization of Casein Fibers by Desamination*

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Abstract

Casein fibers hardened with formaldehyde solutions need further processing to withstand boiling acid dye baths. Studies on desamination of casein fiber at various steps in the spinning process are reported. Desamination of casein fiber increases its resistance to dye baths. Desaminated fiber is given additional stability by treatment with acid-formaldehyde solutions followed by baking at 110°C. Dye uptake of both acidic and basic dyes is reduced by the combined treatment.

PREVIOUS PAPERS from this laboratory have reported studies designed to increase the strength of casein fibers [11] and to develop continuous-filament yarns by pot spinning [12]. Stabilizing casein fibers hardened with formaldehyde so that they can be treated with boiling aqueous acid dye baths without shrinkage or loss of tenacity is a formidable problem, but it must be considered an essential part of fiber production.

Acetylation was used to stabilize the commercial casein fiber Aralac [2]. Papers from this laboratory [3, 12] gave experimental data on the acetylation process for our casein fiber, but pointed out the deficiencies of the process. Because acetylation must be effected under almost anhydrous conditions, the process requires careful control. Also, the use of a flammable hydrocarbon solvent as a diluent for the acetic anhydride makes the process a serious fire hazard. A process in which only aqueous solutions are used for stabilizing casein fibers would obviate this fire risk. A treatment with acid-formaldehyde solutions followed by drying and baking has given moderate stabilization [13], but increasing the stabilization of tensile strengths from 80% to nearly 100% is difficult.

Desamination of casein has been the subject of many reports in the literature [1, 6, 7, 16]. However, because little quantitative information is given, this investigation was undertaken to determine to what extent desamination might be carried and the maximum stability to be obtained from the process.

Apparatus and Methods

The casein fiber used in this work was in the form of a 300-den. 40-filament yarn with about 3 turns Z-twist per in. Its preparation and testing for tenacity have been described elsewhere [12].

To evaluate the resistance to boiling baths used in applying acid dyestuffs, a standard procedure was developed. Two g. of yarn were tied in a loose hank and boiled under reflux for 1 hr. in 80 ml. of solution containing sufficient acetic acid to give pH 4 and 10% sodium sulfate (based on the weight of the fiber). The fiber was rinsed, centrifuged in a small basket centrifuge, and dried at 100°F. Then it was conditioned for at least 2 hrs. before being tested at 50% relative humidity and 73°F. The tenacity obtained after simulated dyeing in this fashion is referred to as "tenacity after boiling."

Equilibrium dye uptake was determined by the method of Fraenkel-Conrat and Cooper [5]. The samples of fiber were ground in a Wiley mill and shaken with the dyes and buffer for 24 hrs. at 73°F in a constant-temperature room. Cross sections were made of fiber dyed in a similar manner, but not ground in the Wiley mill. The fibers did not show ring dyeing, and were uniformly stained across the section.

Reflectances were measured on a fabric knit from the dyed yarn on a 300-needle half-hose knitting machine. The fabric was doubled and redoubled; then the reflectance curve was run on a General Electric

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TABLE I. EFFECT OF TEMPERATURE OF "BLANK" DYE BATH ON TENACITY AND SHRINKAGE OF FIBER

Temperature of dye bath (°C)	Tenacity after dyeing (g./den.)	Loss in tenacity (%)	Denier	Shrinkage in length (%)
Control	1.06	—	275	—
40	1.03	0	305	9.5
50	1.06	0	298	8.0
60	1.00	6	306	10.0
70	0.88	18	340	19.0
80	0.65	39	402	32.0
90	0.63	41	428	36.0
100	0.11	90	519	47.0

recording spectrophotometer. A wave length of 440 mμ was chosen; here the reflectance curve showed the greatest difference for treatment with increasing amounts of nitrous acid. The colors ranged from light yellow to deep orange.

Van Slyke amino nitrogen determinations were made on the solid fiber by the method of Doherty and Ogg [4]. The fibers were ground to pass 60-mesh sieves in the Wiley mill.

Experimental Procedure

To show the effect of temperature in accelerating the loss of formaldehyde from the yarn before it is stabilized, 2-g. samples of the yarn were held in the blank dye bath for 1 hr., but at temperatures increasing from 40°C to the boil. The values for shrinkage in length and loss in tenacity, shown in Table I, reflect the loss of formaldehyde. Rath, Essig, and Abele [14] showed that the formaldehyde driven off in 1 hr. rose from 5% at 60°C to 70% at 100°C.

Desamination can be effected at several stages in the spinning process. Casein can be desaminated by sodium nitrite or nitrous acid before preparation of the spinning solution. If the desaminated casein is not allowed to dry out before it is dissolved in dilute alkali, a solution suitable for spinning can be made. The properties of the resulting fiber are disappointing, however, as the tenacities of both the wet and the dry fibers are lower than those of untreated casein. This result is not unexpected, because selective benzoylation of the amino groups of the casein before spinning, by the method of Mellon, Korn, and Hoover [8], also gives a fiber of low tensile strength. The present spinning method is based on partial hardening with formaldehyde, stretching, and then complete hardening. Covering the amino groups or removing them interferes with the hardening process, and, as a result, less tension can be applied to the tow before it breaks. Stretching is necessary to give greater tenacity [11].

TABLE II. EFFECT OF SODIUM NITRITE IN FINAL WASH BATH AT pH 6 ON STABILITY OF FIBER

Final wash	Tenacity of dry fiber (g./den.)	Tenacity of wet fiber (g./den.)	Tenacity of boiled fiber (g./den.)	Loss of tenacity on boiling (%)
30% Acetate (Control)	1.20	0.34	0.06	95
30% Acetate plus 5% sodium nitrite	1.14	0.33	0.28	75

TABLE III. EFFECT OF INCREASING RATIO OF NITROUS ACID TO AMINO GROUPS ON STABILITY OF FIBER (TREATMENT AT 25°C FOR 2 HRS.)

Ratio of HNO_2/NH_2	Tenacity at 73°F, 50% R.H. After treatment (g./den.)	After boiling (g./den.)	Loss in tenacity (%)	Color
Control	1.12	0.14	88	White
3.33×	0.97	0.59	39	Light yellow
6.66×	1.03	0.61	41	Light yellow
10.0×	1.04	0.64	38	Yellow
13.3×	1.04	0.65	37	Yellow
16.6×	1.04	0.69	34	Orange
33.3×	1.01	0.69	32	Orange
33.3× (16 hrs.)	1.11	0.83	25	Brownish orange

Nitrous acid can be applied in the acid precipitating bath, the stretching bath, or the wash bath used to adjust the pH of the fiber before it enters the pot, but many experiments have shown that only in the last bath can nitrous acid be used without seriously affecting the tensile strength. Comparison with control yarns (Table II) shows that a small improvement in boil-resistance results from this treatment.

After the raw fiber has been further hardened so that it contains 2% formaldehyde, stronger nitrous acid solutions can be applied without affecting the tensile strength. The improvement in boil-resistance caused by the increased desamination is considerable. The nitrous acid, formed by reaction of equivalent quantities of acetic acid and sodium nitrite, is used in excess, based on 0.8% free amino nitrogen in casein. The fiber is treated in a batch process, in which a bath-to-yarn ratio of 30 to 1 is employed. Table III shows that the loss in tenacity on boiling may be cut from 88% to 25% but that the fiber is deeply colored.

Additional quantitative information is needed to show the other effects of nitrous acid on the yarn.

TABLE IV. EFFECT OF INCREASING RATIO OF NITROUS ACID TO AMINO GROUPS ON PROPERTIES OF YARN AND FABRIC (TREATMENT AT 25°C FOR 2 HRS.)

Ratio of HNO_2/NH_2	Dye uptake at pH 2.2 (equiv. dye per 10^6 g. fiber)	Amino nitrogen (%)	Reflectance of fabric at 440 mμ (%)
Untreated	5.3	0.75	63
3.33×	4.1	0.24	31
10.0×	2.5	0.16	13
33.3×	1.8	0.10	9
33.3× (16 hrs.)	1.5	0.05	—

TABLE V. STABILIZATION OF DRY FIBER CONTAINING 2% FORMALDEHYDE BY BAKING IN ACID CONDITION (110°C FOR 30 MIN.)

Impregnating solution	Tenacity of dry fiber at 73°F, 50% R.H. After baking (g./den.)	After boil test (reconditioned) (g./den.)
1% HCl—10% CH_2O	1.08	0.61
2% HCl—10% CH_2O	1.05	0.69
3% HCl—10% CH_2O	1.11	0.70
5% HCl—10% CH_2O	1.08	0.68
None (control)	1.20	0.06

Dye absorption at equilibrium with an acid dye in excess is used as a measure of the relative numbers of basic sites available. The content of Van Slyke amino nitrogen is a measure of the unreacted amino groups left in the yarn which will react with the relatively more-concentrated HNO_2 in the reaction chamber. The increasing depth of color of the fiber is a considerable drawback, because it must be reduced by bleaching with dithionites, for example, before the fiber can be dyed with light shades. These qualities are summarized in Table IV.

The reduction in dye uptake parallels the decrease in Van Slyke amino nitrogen, but the change in amino nitrogen content is greater than that in acid dye uptake, for the latter reaction is related to the sum of all the basic groups present. The absorption of a basic dye, Safranine O, was not increased by desamination, as had been reported for wool [15].

TABLE VI. FURTHER STABILIZATION OF CONTINUOUS-PROCESS DESAMINATED YARN BY BAKING IN ACID CONDITION (110°C FOR 30 MIN.)

Impregnating solution	Tenacity of dry fiber at 73°F, 50% R.H. After baking (g./den.)	After boil test (reconditioned) (g./den.)
1% HCl—10% CH_2O	1.02	0.78
2% HCl—10% CH_2O	0.99	0.89
3% HCl—10% CH_2O	1.04	0.84
5% HCl—10% CH_2O	0.99	0.81
Control (desaminated)	1.14	0.28

TABLE VII. BOIL-RESISTANCE AND REFLECTANCE OF FIBER STABILIZED BY FORMALDEHYDE, BAKING, AND DESAMINATION (2.3 RATIO, 25°C, FOR 2 HRS.) AND SUBSEQUENTLY BLEACHED VERSUS THOSE OF ACETYLATED FIBER

Tenacity at 73°F, 50% R.H. Original fiber (g./den.)	Treated and bleached fiber (g./den.)	Boiled fiber (g./den.)	Reflectance of boiled fiber at 440 mμ (%)
1.1	1.1	0.86	43
1.2	1.0	0.80	48
1.0	1.0	0.90	48
	Acetylated	Acetylated	
1.2	0.94	0.61	—

Previously reported work [13] has shown that treatment of finished fiber containing 2% formaldehyde in an acid-formaldehyde solution, followed by drying at increasing temperatures, produces a moderate degree of stability to boiling in acid dye baths. As shown in Table V, for the type of fibers used in this work, the acid strength could be varied from 2% to 5% without changing the strength of the treated fiber, but additional increase in acid concentration lowered the strength after treatment and the boil-resistance.

The advantage of this method over desamination lies in the resulting color of the product. If sulfuric acid is used instead of hydrochloric acid, a lighter color is obtained, but the fiber must be baked at a slightly higher temperature to obtain the same degree of stabilization. It remained to be proved whether the two stabilization processes were additive, or whether one would cancel the effect of the other. The yarn described in Table II, which showed about 0.16% amino nitrogen by the Van Slyke determination, was given the acid baking treatment, and the amount of acid was varied within the same limits as before. Table VI shows the improvement in boil-resistance.

The residual color may easily be removed by dithionite, as the acid-formaldehyde solution seems to have some bleaching action of its own. The loss of tenacity of the stabilized and bleached yarn when boiled is only 10%. The combined process represents an improvement over the acid baking process, and the color imparted to the yarn is less than that

TABLE VIII. MODIFICATION OF PROPERTIES OF YARN BY COMBINING CHEMICAL TREATMENTS

Treatment	Tenacity at 70°F, 50% R.H. (g./den.)	Tenacity of wet fiber (g./den.)	Amino N (%)	Acid dye absorption (equiv. dye per 10^6 g. fiber)	Basic dye absorption (equiv. dye per 10^6 g. fiber)	Water absorption† (%)
None	1.21	0.40	0.8	4.95	12.1	33.0
Desaminated*	1.10	0.49	0.05	1.85	11.2	30.4
Acid-CH_2O + baking at 110°C	0.96	0.31	0.15	4.1	5.65	31.0
Combined treatments	1.11	0.51	0.09	1.80	5.55	28.8
Acetylated	0.94	0.31	0.09	1.95	12.8	36.5

* 16 hrs. at 25°C, 33.3/1 ratio HNO_2/NH_2.

† Imbibed water not removed by centrifuging for 5 minutes at 1,000 relative centrifugal force.

shown in Table IV for the treatment in which the yarn after hardening was desaminated to 0.24% amino nitrogen.

Desamination can also be carried out as a batch process before the fiber is stabilized by acid baking with formaldehyde, as previously reported [13]. Table VII shows tenacity and reflectance measurements of 3 typical samples. Even after boiling, the fiber had a tenacity of 0.8 to 0.9 g. per den., and its reflectance of 48% can be compared with the value of 63% for the untreated fiber. Acetylation of these 40-filament yarns gives less effective stabilization than acetylation of the 150-filament yarns previously reported [12].

Table VIII contains comparison of the other effects of the stabilization process. Tenacity of the wet fiber was improved by intensive desamination. The color produced by this desamination could not be fully bleached. Dye absorption for both acid and basic dyes was decreased by the combined process. The tenacity of the colored yarns was stabilized at as much as 0.96 g. per den. after boiling. Water absorption was decreased by desamination and acid baking. Surprisingly, in contrast to results reported for earlier work [3], acetylation in a solvent increased the water absorption. A different method of acetylation was used [12] to avoid excessive loss of tenacity. Even under these conditions, acetylation may remove 0.5% formaldehyde.

Discussion

When nitrous acid reacts with casein, the ε-amino groups of lysine are rapidly converted to ε-hydroxy groups. The arginine, tyrosine, and tryptophane contents also enter into the reaction. The reaction with tyrosine is probably responsible for the color produced by desamination, because nitroso derivatives of tyrosine have been demonstrated [9].

The effect of desamination in increasing the strength of the wet fiber and its stability to boiling is best explained by the addition of new cross bonds. The stress-strain curve for the wet fiber shows a definite yield point, as compared with that of the unmodified fiber. The bonds are probably diazo linkages [10]. Additional support is given to this theory by the fact that when fibers stabilized by desamination are reduced with dithionite to remove the color, their strength after boiling is decreased slightly by this treatment.

The nature of the chemical reactions produced by baking after acid and formaldehyde treatment has not been demonstrated. The reduction in basic-dye binding capacity indicates that Koch's suggested mechanism of carboxyl group esterification with methylene glycol might be partially correct [7]. In addition, the reduction in acid-dye absorption follows the decrease in Van Slyke amino nitrogen. It is probable that these acid-resistant cross bonds involve some of the amino nitrogens in the fiber.*

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*NOTE: The mention of any specific equipment in this paper does not imply that these products are endorsed or recommended by the U. S. Department of Agriculture over others not mentioned.

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Special Dyeing of Cotton on the Seed Gives Visual Evidence of Changes During Fiber Development*

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This is the second in a series of papers on a special method of dyeing cottons differentially to show differences between them. The main purpose of this work has been to develop techniques for identifying thin-walled (immature) cotton fibers, and for showing their amount and distribution in the presence of thick-walled (mature) fibers. Such special dyeing has proved useful to a number of cotton manufacturers and finishers in problems involving fiber-wall thickness. The present paper is an account of the use of differential dyeing in another way to furnish visual evidence of a fundamental submicroscopic change in cotton as it dries when the boll opens on the plant, and to indicate structural differences between thin- and thick-walled cotton fibers. The work contributes also toward the explanation of the differential-dyeing effect.

Abstract

A process of differential dyeing employed to distinguish between thick- and thin-walled cotton fibers has now been utilized to show visually that the drying of normal cotton fibers for the first time—as when the boll opens in the field—greatly affects their dyeing properties. The effect was observed as a pronounced color difference when one lock from a nearly mature boll, cut open in the laboratory, was dried and another lock was kept wet, and both were dyed in the same dye bath at the same time.

The dried cotton dyed mainly red and the undried dyed green. The change in the cotton cellulose which caused the difference is undoubtedly submicroscopic, and takes place in addition to the changes visible in the microscope which are familiar in fibers that have dried normally on the plant. A significant feature of the submicroscopic change can be inferred from the dyeing behavior considered in relation to current views of the mechanism of direct dyeing—that is, undried fibers from a cotton boll are shown by a new technique to be more porous than fibers which have dried in the boll, and the thin-walled fibers in ordinary cotton are similarly more porous than the thick-walled fibers, at least while wet in a hot dye bath. It follows that the differential-dyeing effect with cotton fibers is determined by cellulose structure in combination with specific properties of the two dyes employed.

* Report of a study made under the Research and Marketing Act of 1946.

† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Introduction

A method for distinguishing thin-walled cotton fibers (commonly called immature) from thick-walled fibers (mature) was recently described [6]. It is based upon dyeing the cotton in a bath containing two direct cotton dyes, a green which tends to color the thin-walled fibers selectively, and a red which tends to color the thick-walled fibers selectively. Pronounced gray and reddish colors obtained in dyeing can be made to appear in much greater contrast as green and red by after-treatment with boiling water, which constitutes virtually a partial and selective stripping.

The over-all colors of samples of different cottons dyed differentially may also differ greatly because nearly every cotton consists of a mixture of thin- and thick-walled fibers and the final color will depend upon their proportions in the mixture. Actually, however, the observed differences do not depend merely upon thickness of cell wall but also upon some factor more fundamental in cotton fiber structure.

Sensitivity of the technique to influences other than wall thickness has now been utilized to detect changes in the cotton in its final stage of development—that is,

as the boll opens and the cotton dries. The purpose of this report is primarily to describe the resulting color effects, with supplementary observations from other direct dyeings and from mercerization, as visual evidence that pronounced changes do occur in the cotton cellulose; and then to offer suggestions regarding the nature of these changes, as implied by the dyeings.

Methods Employed

The description of the special method of differential dyeing [6] will be repeated here for convenience.

Samples of cotton are dyed comparatively, all in the same bath at the same time, each sample being loosely enclosed in a small bag made from bleached open-mesh gauze of, say, 28 × 24 thread count. After weighing, the cotton is entered into a boiling bath made up with distilled water to 40 times the weight of cotton and containing 1.2% Diphenyl Fast Red 5BL Supra I (Geigy) (Color Index No. 278) and 2.8% Chlorantine Fast Green BLL (Ciba) (no C. I. number), calculated on the weight of all the cotton (samples plus gauze). When the cotton is to be dyed while still on the seed, as in the experiments to be described below, an allowance for the weight of seed can be made if it amounts to an appreciable proportion of the total weight. Otherwise the dyeings will merely be darker as greater relative amounts of seed and less cotton are present.

After dyeing for 15 min. at the boil, the cotton is lifted out and 2½% of its weight of C. P. sodium chloride is stirred into the dye bath. The cotton is re-entered into the bath for 15 min., then lifted out again, and a second portion of 2½% sodium chloride is added. The dyeing is continued at the boil, with the addition of water if needed to maintain the original volume, for a total of 45 min., after which the cotton is lifted, drained or hydroextracted, cooled, and then washed well in two changes of cold distilled water in the proportion of 50 parts of water to 1 of cotton.

After the removal of excess cold wash water, the dyeings are dipped into vigorously boiling distilled water (50:1) for a definite length of time, usually exactly 30 sec., with stirring, then lifted, drained, squeezed or extracted, and washed in cold water as before. The hot washing, which is not in accordance with usual direct-dyeing practice, removes excess red dye but relatively little green dye, thus eliminating grayness and resulting in more clearly defined red and green colors.

After final wringing, the dyeings are removed from the gauze bags and allowed to dry in the open air or with moderate heat. Thick-walled, or mature, cotton as normally picked is colored to a pronounced red; and thin-walled, or immature, cotton is usually colored to a distinct green. The extremes of color obtainable are represented approximately by the reddest and greenest areas in Figure 1 of the reference cited [6], the two very different colors being obtained in the one dyeing process.

The colors of the red-dyed and green-dyed cottons, even though in strong contrast, usually are considerably different from the "self shades" of the individual dyes. Each tends to be somewhat duller because the red and green, approximately complementary colors, can combine to make gray, and the predominating dye on the fibers is somewhat affected by the presence of some of the other dye on the same fibers. When tufts of red and green fibers taken from such dyed cotton were compared directly with the charts in the *Munsell Book of Color* [7], the greenest color obtained was found to correspond approximately with blue-green, value 5/ and chroma /4; and the reddest, with red-purple, value 5/ and chroma /8.

Keeping the cotton on the seed has the obvious advantage of showing the relative positions of the fibers which dye to different colors. Careful hand-wringing, or the use of a centrifuge, is suggested in order to keep the seeds intact, since the boiling dye bath softens them and they are likely to be crushed and mixed with the cotton if put through a wringer.

For the experiments which included redyeing, the green-red dye combination was readily stripped with commercial sodium hydrosulfite, 5% on the weight of all the cotton, in 20 or 30 times its weight of water, usually within 5 min. if treated at the boil. For consistent results, it has been found best to dry the stripped cotton before redyeing (except when it must be kept wet to meet other requirements of the experiment). When successive dyeings and strippings are to be made, it is advisable to dye as many as possible of the samples which are intended for final comparison all at once in the last dye bath in order to avoid the effects of slight, but almost unavoidable, differences from one dyeing to another.

Dyeings were also made with individual dyestuffs such as those frequently used to bring out differences in dyeing capacity of cottons, uncomplicated by differential effects—namely, with a direct sky blue 6B (Color Index No. 518) and a direct fast blue 4GL [reference

1, Prototype 26]. A method which is usually satisfactory is to dye at the boil with 1% color (based on the weight of the cotton), with the addition after 10 min. of 10% salt and of a second 10% after another 10 min., continuing up to a total dyeing time of 30 min. The resulting dyed cotton is then washed well in cold water and dried. Relative depths of color were estimated by visual comparison with special dyeings made with known amounts of the blue 4GL, each dyed to exhaustion.

For mercerization, cotton fibers still on the seed and perfectly free to swell were immersed for several minutes at room temperature in sodium hydroxide of 22% concentration containing 1–2% of a proprietary "penetrating" agent to assist the wetting of the dry raw cotton by the alkali. The cotton was then washed well with distilled water, neutralized with dilute acetic acid, washed again, and used while still wet.

Observations on the Dyed Cottons

When a boll which appeared to be nearly ready to open naturally on the plant was picked and opened under water and one lock (the cotton in one section of the boll, with seed) was kept wet while another was dried, and then both locks were dyed together in the differential dye bath and stripped with boiling water, the fibers that had not been predried all came out green, whereas those dried before dyeing came out mainly red, with green-dyed fibers present in the latter only in accordance with the number not having normal secondary-wall thickening. If the green-dyed cotton (never previously dried) was then dried, the color stripped with hydrosulfite, and the cotton dyed again in the same way as before, it colored red (with some green fibers) just as the original dried and dyed lock did. On the other hand, when another sample that had not been predried was dyed (green), stripped, and dyed again, without any intermediate drying, it colored green just as it had before. These observations are summarized in Table I.

The green that results from dyeing undried cotton is usually much darker than the green of the ordinary differentially dyed thin-walled fibers, being typically represented by Munsell's [7] blue-green of value 2/ and chroma /2 to /4.

In the experiments reported here, more than a dozen cottons were dyed "wet and dry" with consistent and striking results. When locks from comparable bolls which had been open for a short time on the plants were included in the dyeings, these came out somewhat redder than locks dried from the bolls picked at a slightly earlier stage of growth and opened in the laboratory. Late-season bolls which were not well developed gave less pronounced contrasts when dyed wet and dry.

TABLE I. SUMMARY OF OBSERVATIONS FROM DIFFERENTIAL DYEING (COTTON ON THE SEED)

	Color after treatment indicated				
State of cotton	Dyed	Dried	Not dried	Stripped	Dyed again
Original, moist from boll	Green	Green	—	White	Red
Original, moist from boll	Green	—	Green	White	Green
Dried from boll	Red	Red	—	White	Red

Dyeings by the differential technique were supplemented by experiments more nearly like ordinary direct-dyeing procedures. A lock of cotton from a boll picked before it opened on the plant was dyed without drying and another was dyed after drying, both in one bath as before, but with a single blue dyestuff. Instead of contrasts in color there were differences in depth of color only, the cotton which had not been dried being much darker. When a comparable lock of mercerized cotton was included, the cotton dried from the boll before dyeing came out lightest and the mercerized lock darkest, the depth of color of the cotton dyed without previous drying being intermediate. The differences in depth of color from one sample to another in the series were of the order of 50% of that of the dyeing of middle depth (cotton dyed without previous drying).

The colors of the mercerized cottons dyed by the differential technique were also very dark but diverged considerably from the usual pronounced red and green.

The difference in color between cottons dyed differentially before and after drying from the boll suggested that, possibly, crystallization of original amorphous cellulose in the cotton fiber, and perhaps orientation, caused by stretching fresh moist cotton fibers [2] might affect the dyeing. But the stretching of samples of undried fibers of several varieties by hand failed to cause perceptible differences in the dyed shades as compared visually with the shades of corresponding unstretched cottons dyed at the same time. However, this negative result does not necessarily mean that there was no increase in crystallinity or in orientation upon stretching, but only that this

particular dyeing process was not sensitive to such changes if they took place.

Relationships Between Color of Dyed Fiber and Cellulose Structure

As shown in the earlier publication [6], when cotton which had been removed from the growing boll after the onset of normal secondary-wall thickening, but before the boll would have opened naturally, was washed in hot water and dried and then dyed by the differential technique, the fibers or parts of fibers which had become thickened were colored to a pronounced red, while fibers not yet thickened came out green. Similar observations on several cottons showed that the thickened fibers tended to dye just as they would if they had been allowed to grow until the boll opened naturally, and that thin-walled fibers were colored green whether they had been taken from a boll picked prematurely or from one fully grown and opened on the plant. It follows, then, that the test is independent of the maturity of the cotton in the physiological sense, although it will, in general, differentiate mature and immature fibers as defined by wall thickness.

However, although thick- and thin-walled fibers usually dye consistently red and green, respectively, the selectivity is not actually a direct function of wall thickness, as is clearly shown by the special dyeings of dried and undried locks of cotton from the same boll. Here, wall thickness could not have been the main determining factor in their coloring red and green because in normal locks from a given boll the wall thicknesses of the fibers are approximately the same (except that in the experiment one was swollen more than the other at the time of dyeing).

It follows from the present work that the *drying* of the cotton from its natural wet state in the boll is the immediate cause of the change in its sorptive properties for particular dyestuffs. Since dyeing effects obtained on such cotton which had been dried in the open air were found to be the same as those obtained on cotton dried with heat, it is evident that the change is not due merely to the heat during drying, and also that the same change must take place in cotton which opens naturally and dries in the field. In addition, the heating of undried cotton in the dyeing and stripping baths (to nearly as high a temperature as in the hot drying) made no apparent change in its dyeing properties, as was shown by redyeing cotton which had never been dried—*i.e.*, it still dyed green. Hence, the differential coloring of the originally moist and the dried cottons is almost certainly due in large part to submicroscopic structural changes in the cellulose of the fibers which occur upon drying—to something fundamental in the development of normal cotton in addition to the familiar changes visible in the microscope after the fibers have been dried for the first time.

If we reason on the basis of the dyed fibers the differential coloring of which depends so largely upon structural change in the cotton cellulose incident to drying, it is an almost inescapable conclusion that there is similarly a structural difference between thick- and thin-walled fibers in ordinary cotton.

Although the differential-dyeing effect must depend greatly upon cellulose structure, it unquestionably depends also upon the mechanism of the direct dyeing, and when both of these are taken into account, further inferences may be drawn concerning the relationship between color of dyed fiber and cellulose structure.

In direct dyeing [3, 9], it appears that the dyes enter water-swollen cellulose fibers by a process of diffusion through "pores" of such sizes that large and small dye molecules may not diffuse through them equally freely. The dyeing proper consists in the attachment of dye molecules to surfaces which are mainly within or around the amorphous portions of the cellulose, which are reached through the pores. The hot-water stripping employed in differential dyeing consists in the removal of dye molecules entrapped in the cellulose or attached to it by their diffusion outward through the same pore system. Hence, both the exact mechanism of dyeing with specific dyes and the fastness of such dyes to hot water depend upon the affinities of the dyes for the cellulose and upon the ease of movement of their molecules through its pores.

The two dyes employed in the differential dyeing differ greatly in respects which are significant for that technique. As is well known, the green dye [5] has a molecular weight about twice that of the red [8], and it dyes much more slowly, as has been reported for its use on rayon [4]. Special experiments have shown also that the green dye is absorbed more slowly by cotton than is the red.

It seems natural to consider that the possible differences between the fibers or the celluloses rather than differences between the properties of the dyestuffs are the underlying cause of the differential-dyeing effects, because the state of the cellulose at the

time of dyeing determines the accessibility of its internal adsorbing sites to the dye molecules.

Since the wet cotton in the unopened boll is highly swollen, it has a much more open structure than it would have after drying. This undried cotton no doubt also retains a relatively greater degree of swelling in the dye bath than is attained by the cotton that has been dried and rewet. This greater degree of swelling is unquestionably a determining factor in the dyeing because it makes available more dyeing surface or a greater number of adsorbing sites; and it no doubt allows much easier access of the large, green dye molecules to the interior of the fibers. Hence, if we reason from dyeings to fiber properties, the relatively dark green dyeing of the undried cotton fibers implies greater openness or porosity, which is indicated also by their cross sections, which are green throughout, showing penetration by the large, green dye molecules.

Similarly, the green color of the cross sections of thin-walled fibers found in ordinary cottons which had been dyed differentially indicates that these fibers are more porous, at least while in the dye bath, than are the thick-walled fibers which had been dyed at the same time, since the latter do not show the presence of green.

Furthermore, when a mature and an immature cotton were dyed with the green dye alone for 5 min. in a suitable bath, the thin-walled fibers of both were dyed throughout, as shown by cross sections, indicating that these fibers could be readily penetrated by the large, green dye molecules, whereas the thick-walled fibers were not penetrated appreciably. These observations seem also to confirm the view that the thin-walled fibers are more porous.

Acknowledgment

Some of the cottons used in the work described here were furnished by the Louisiana State Agricultural Experiment Station through the kindness of Dr. C. C. Murray and of F. W. Self. Others were furnished by the U. S. Cotton Field Station at Knoxville, Tennessee, through the kindness of Dr. D. M. Simpson.

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(*Manuscript received September 19, 1949.*)

Letters to the Editor

Examination of Rayon Cross Sections with the Electron Microscope in Conjunction with Supplementary Light-Microscopic Observations*

INSTITUTE FOR CELLULOSE RESEARCH OF THE AKU AND AFFILIATED COMPANIES
Utrecht, Netherlands
October 27, 1949

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Previous attempts to investigate sections of synthetic fibers with the electron microscope have not been very successful. It is understood that sections suitable for examination should be very thin—0.5 μ, or preferably thinner.

In this journal Horio *et al.* published electron micrographs of wedge-shaped sections of thick laboratory-spun model fibers from viscose, obtained with an ordinary microtome [1]; in a later paper, Earle and Minkin [2] presented micrographs of sections made with the high-speed ultramicrotome. These authors succeeded merely in obtaining fragments of sections and used fibers previously coated with gold in order to be able to recognize the fiber surface in the fragments obtained. The published pictures obviously reveal that considerable mechanical damage has been done to the material in the cutting operation, and the pictures therefore would seem to be of very limited interest.

Dr. Bretschneider in Utrecht recently succeeded in obtaining almost perfect 0.2–0.5 μ sections of various biological objects with an ordinary microtome of very simple construction [3]. With the advice and kind assistance of Dr. Bretschneider, we succeeded in obtaining reasonable results with paraffin-embedded viscose fibers by using an ordinary Leitz sledge microtome, setting it to cut sections of 1 μ thickness. In making a great number of cuts many sections were obtained which appeared to be much thinner than 1 μ and suitable for examination in the 90 KV Electron Microscope. It is true that whole sections thin enough for use were not observed, but it was not difficult to find well recognizable section fragments in the preparation.

One of several pictures obtained is reproduced in Figure 1 (magnification, 4,000 ×). It shows a fragment of a section of a viscose fiber taken from a yarn of the tire-cord type; lying next to it is a much thicker fragment (in which no details are revealed). The thin fragment clearly shows the lobed surface of the filament and the presence of numerous small voids in a rather thick cortical layer of the fiber.

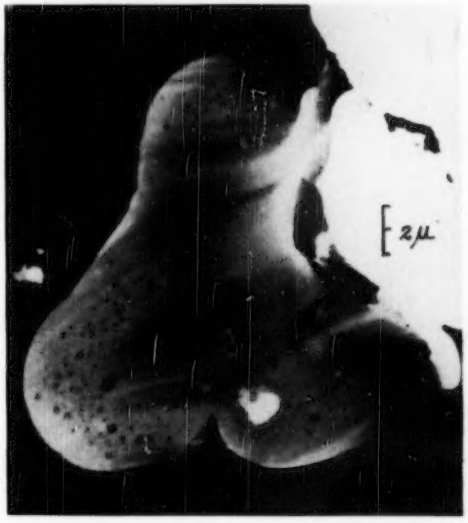

FIG. 1. *Electron micrograph (4,000 ×) of a section fragment.*

* Communication No. 62 from the Institute for Cellulose Research of the AKU and Affiliated Companies, Utrecht, Netherlands.

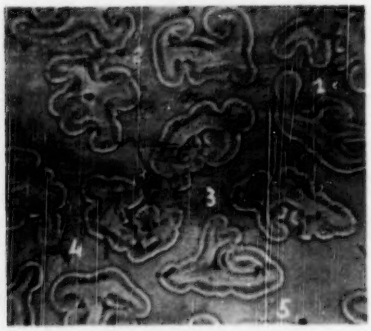

FIG. 2. *Ordinary micrograph of sections taken with a narrow cone of light.*

FIG. 3. *Micrographs of sections taken with dark-field illumination.*

FIG. 4. *Phase contrast picture of sections immersed in a liquid with* $n = 1.531$.

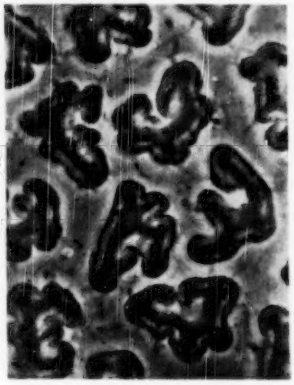

FIG. 5. *Phase contrast picture of sections immersed in a liquid with* $n = 1.495$.

The thickness of this layer corresponds to about that of the fiber skin as revealed by the Victoria Blue staining technique [4]. Other pictures obtained showed the same structure. The micrograph represents a "negative image" picture (like the one on the original film, which was first printed on diapositive film; a paper print of the latter is reproduced here).

The occurrence of numerous small voids in the cortical layer is just what was expected from the examination of ordinary 6 μ sections of the same fiber with the light microscope. The observed porosity is probably identical with the phenomenon of so-called "milkiness," which is well known in viscose rayon manufacturing.

Figure 2 is an ordinary micrograph of 6 μ sections of the same fiber immersed in a liquid with $n = 1.535$ and taken with a very narrow cone of light.

Figure 3 is a dark-field micrograph and Figures 4 and 5 are pictures taken with the phase contrast microscope of the same sections immersed in liquids of slightly higher and slightly lower refractivity than that of the sections.

In Figure 4 the circumference of the sections shows bright contrast, and in Figure 5, dark contrast against the liquid. The occurrence of gas-filled voids (which, of course, should appear in bright contrast) is best revealed in the picture taken

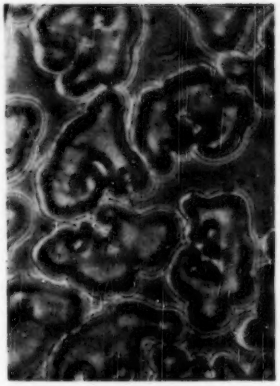

FIG. 6. *Phase contrast picture of sections swollen in water* (n = 1.333).

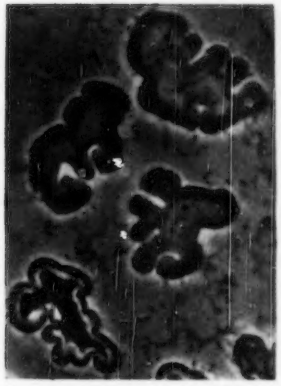

FIG. 7. *Phase contrast picture of sections immersed in a pyridine-water mixture with* n = 1.499. *Some sections are swollen, others not yet.*

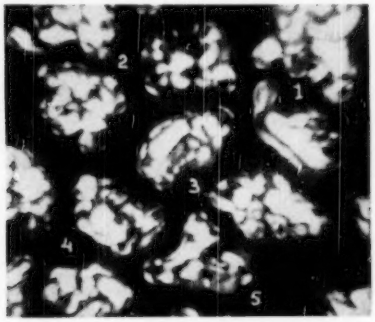

FIG. 8. *Same sections as in Figure 2 photographed between crossed Nicols.*

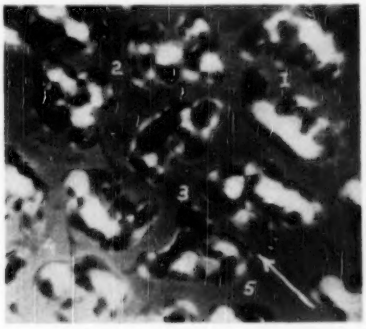

FIG. 9. *Same sections as in Figure 2 photographed between crossed Nicols and compensated in the direction of the arrow.*

with a liquid of lower refractivity in the form of not well resolved little white specks. These can also be detected in Figure 2 as grayish zones with a not sufficiently resolved structure.

From Figures 2 and 5, as well as from the electron micrograph in Figure 1, it is further apparent that the outermost part of the cortical layer is free of voids and that the voids begin to occur at a depth of about 1 μ below the surface. The thickness of the so-called fiber skin (as revealed by staining techniques) is about 3 μ. It coincides with the bright outer zone in Figure 4.

In Figure 6 are shown (also undyed) sections of the same fiber lying in water and photographed with the phase contrast microscope. The difference in refractivity between the swollen section and the water being very considerable, diffraction rings appear at the section circumference.

Inside the swollen sections it is seen that the skin appears in dark contrast against the core, indicating that the optical density of the former is greater than that of the latter. The "milkiness" has entirely disappeared in the swollen sections, the voids being either closed or filled with water. Figure 7 shows sections after immersion in a 12:1 mixture of pyridine and water ($n_D^{20} = 1.499$) in which swelling is slow and less than in water. Some sections in the picture are swollen, others not yet. The latter still have the appearance of those in Figure 5.

That the inner structure of the rayon fiber is very complicated and that the use of as many techniques of microscopical examination as possible is required for its study are also revealed by examination in polarized light. Figure 8 shows the very same sections as Figure 2, photographed between crossed Nicols, and Figure 9 shows the same sections after superimposing a compensating birefringence in the path of the light, with the largest refractive index in the direction of the arrow. Patches having an orientation parallel to the arrow remain bright, whereas the light transmitted by patches with an orientation perpendicular to the direction of the arrow is extinguished. It will be seen that the fiber skin has an orientation perpendicular to the fiber surface in those regions where no excessive folding and lobing have occurred. In the lobes the situation is more complicated. (In order to facilitate location of the individual sections in Figures 2, 8, and 9, numerals in white have been drawn in.)

The continuation of this work with other types of viscose fibers is planned.

The author is indebted to the Institute for Electron Microscopy in Delft for taking the electron micrographs.

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Very truly yours,
P. H. HERMANS

"The Fine Structure of Cotton Fibers from Density Measurements"

INSTITUTE FOR CELLULOSE RESEARCH OF THE AKU AND AFFILIATED COMPANIES
Utrecht, Netherlands
November 18, 1949

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In a recent paper entitled "The Fine Structure of Cotton Fibers from Density Measurements," H. Wakeham (TEXTILE RESEARCH JOURNAL **19**, 595 (1949)) has reported that values for the density of previously cut cotton fibers when measured in benzene tend to be slightly higher than those for whole fibers. Obviously, more of the tiny porous channels within the fiber become accessible to the liquid after cutting.

Wakeham correctly states that this fact may affect the estimations of the crystallinity figure made by the present author from density data obtained on whole fibers.

It is regrettable that Wakeham has not indicated the fluctuations found in his single determinations, but one may deduce from his paper that the average density figures given are significant to about 5×10^{-3}.

The average figure found for cut native cotton in benzene then amounts to 1.56. If this figure is substituted for 1.55 (previously used for the estimation of the crystallinity of cotton) the percentage found is about 70% instead of about 60% (the specific volume of crystalline cellulose again being taken as 0.628 and that of amorphous cellulose as 0.668).

Since the figure derived from x-ray measurements (*J. Polymer Sci.* **4**, 135 (1949)) is 70%, Wakeham's data lead to improved agreement.

Very truly yours,
P. H. HERMANS

INDUSTRIAL SECTION

The Determination of Cotton Textile Dusts in Air

Leslie Silverman and Frederick J. Viles, Jr.

Department of Industrial Hygiene, Harvard School of Public Health, Boston, Massachusetts

Introduction

Air contamination in cotton textile processing is a hygienic and nuisance problem. In a recent review of the literature, Caminita and others [1] described the hazards of exposure to cotton dust as related to affections of the respiratory tract. These authors believe that exposure to cotton dust is an industrial hygiene problem of recognized importance, and the magnitude of the nuisance problem is well known to individuals who have had occasion to investigate a cotton textile plant.

Atmospheric pollution in cotton processing is caused by foreign materials and short cotton fibers present in ginned cotton, which are dispersed into the air during cleaning and subsequent processes. The undesirable material in ginned cotton as it is received at the mill consists of fragments of cotton leaf and seeds and also neps, noils, soil, and inorganic dust particles. All of these materials are removed before the cotton is processed or spun into yarn. The principal materials which contaminate air are: "pepper trash," consisting of small leaf particles and plant fragments; inorganic dust, consisting of inorganic materials carried on the cotton and leaf; and short cotton fibers, usually called lint * by laymen. There may be several other contaminants in the textile-plant atmosphere which become entrained by the cotton during growth—such as insecticides, fungi fragments, and bacteria. During cleaning, these, too, may be dispersed into the workroom air.

The amounts of waste materials (substances other than proper-length cotton fibers) in baled cotton can be considerable. It is well known that the amount of trash in cotton depends principally upon the cotton grade. Data of the U. S. Department of Agriculture [9] show that average picker and card waste (in percent of total cotton weight) varies from 5.5% to 18.8% for the ten grades of cotton. Average cottons encountered in yarn mills usually have between 6% and 8% waste (including organic and inorganic trash as well as short cotton fibers). When the separated material is dispersed into the air, it has been found [6] that organic trash and inorganic dust constitute a much larger percentage of the total air sample. Such samples taken in opening rooms have from 5% to 50% organic trash and from 7% to 30% inorganic dust. Ratios of the percentages of organic trash and inorganic dust in the air to those in the cotton being processed average approximately 12 and 14, respectively. This increase is attributable to air separation, which acts as a classifying process since undesirable constituents of raw cotton are more easily air-borne than yarn-length fibers are.

The effects on the human system of exposure to dust and lint from cotton contaminants and fiber are acute or chronic. The acute disease, called "cotton mill" or "Monday fever," is a problem for workers exposed to dust from opening, picking, and carding operations. It is a non-disabling, temporary reaction which disappears after a day, but limited resistance is acquired by daily exposure. After prolonged absence, however, the reaction can recur. The chronic condition, known as byssinosis (cotton-worker's pneumoconiosis), is found in workers exposed to cardroom and opening-room atmospheres for periods of from 15 to 25 yrs. A greater number of cases have occurred in cardroom operatives because of exposure to higher concentrations of fine dust.

* At the gin, the term "lint" is commonly used to denote the whole cotton fiber after separation from the seed.

Our investigations have shown that there is a definite relationship between total concentration of contaminants in the atmosphere and the incidence of the acute disease. When the total concentration of contaminants in cotton cleaning operations is maintained below 5 mg. per cu. m. of air, it has been our experience that there are no complaints of irritation or fever. Undoubtedly, the incidence of the chronic disease is also related to concentration of contaminants in the air. In order to adequately control the health hazard, therefore, it is essential to have some knowledge of atmospheric contamination in the working environment.

The purpose of this article is to describe methods of determining quantitatively the components of cotton textile dusts in the air.

Determination of Total Air Contamination

Few data have been reported in the literature on actual amounts of dust found to be present in workroom air during cotton processing. The review mentioned above [1] does cite investigations in which dust counts were made. Dust counts have been taken in mills in this country and in England with the impinger, konimeter, Owens dust counter, and the thermal precipitator. Russian investigators [1] report dust concentrations in mg. per cu. m. of air, but no mention is made of the technique employed. Two other Russian investigators [1] reported dust concentrations in mg. per ml. In the meager literature on total air contamination, no attempt has been made to fractionate any of the airborne dusts into components in field sampling other than by using instruments which are selective.

We found in early investigations of this problem that impingement-type instruments [2] are unsatisfactory, since they indicate only a portion of total contamination and possibly only a certain percentage of the inorganic dusts present. Large lint fibers and leaf-trash particles which are light and easily airfloated accumulate at the inlet to the nozzle of the grab-sampling impingement instruments. In the Greenburg-Smith or midget impinger they are difficult to wet and also to count.

In early measurements we employed the M.S.A. (D.C.) Electrostatic Precipitator,* but found that long periods of sampling were necessary. English investigators at The Shirley Institute [3] use an A.C. precipitator as described by Drinker and Hatch [2], but several hours of sampling are necessary to obtain enough material to weigh accurately. They have used the thermal precipitator for obtaining dust counts because their investigations also showed that impingement instruments were unsatisfactory.

Filtration procedures appear to be simple and accurate for obtaining representative samples of total air contamination. For this purpose, the high-volume, high-efficiency sampling and weighing procedure described in a recent article [7] is rapid and direct. By means of this apparatus a weighable sample is collected on a pleated paper filter within 10 min. No appreciable gain of filter weight within this period indicates dust concentrations below 0.02 mg. per cu. m., which is considered negligible. The pleated filter is analyzed for total contamination by direct gravimetric analysis, filters are weighed before and after sampling, and the concentration of contaminants in the air is calculated from the weight gain for a measured volume of air. Weighing difficulties due to adsorbed moisture on the large-surface pleated cellulose filter are minimized by weighing at 110°C in a modified textile balance, using filter blanks to correct for humidity variations.

Separation of Components of Textile Dusts

A study of the literature indicates that it is desirable from hygienic considerations to separate the components of cotton textile dust. The contaminants can be divided into three groups: (1) cellulose from air-borne cotton fibers (lint); (2) organic trash, consisting of organic materials other than cotton lint and principally from leaf, seed, and plant fragments; and (3) inorganic dusts from soil and materials carried by raw and baled cotton from the fields and the gin, and dusts picked up during shipment. Further separation of these materials is difficult and unnecessary.

These three components are also convenient for engineering studies of the cleaning efficiency of textile processing machines. A large portion of inorganic dust is removed from the opened cotton bale by shaking and handling. However, lint and organic trash are difficult to separate because of the tenacious nature of cotton fibers, which enmesh short linty fibers and the large organic or "pepper trash" particles. A machine which is efficient in eliminating inorganic dusts may be inefficient in removing organic trash or fine lint. Air analyses in the vicinity

* Manufactured by Mine Safety Appliances Co., Pittsburgh, Pa.

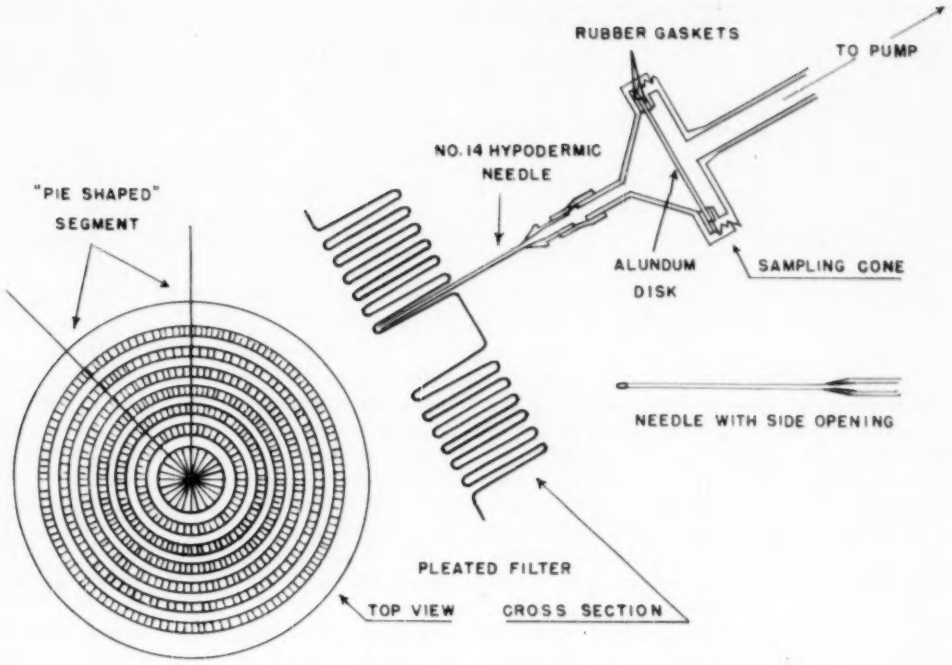

FIG. 1. *Filter-stripping apparatus and sampling needles.*

of machine operations and analysis of the cotton entering and leaving a machine may thus be used to ascertain the amount and the nature of air contamination and the efficiency of the machine cleaning performance.

Another separation is made in air samples taken in weaving rooms, where spun cotton yarn, previously treated with sizing materials, is woven into cloth. Almost all organic trash and inorganic dust have already been eliminated and atmospheric contamination is from short cotton fibers called "fly" and small particles of sizing or starch. Here it is possible to separate the fly from the size particles.

Analysis for each of these components (organic trash, inorganic dust, cotton, and starch) can be carried out on air samples, using single pleated filters. Starch is not usually determined except in weaving-room samples. With this exception, analysis for two of the components permits evaluation of the third by difference, since the sample is separated into three parts.

Analysis for one component often interferes with analysis for other components and corrections are necessary. Organic trash contains cellulose; hence, analyses for cellulose (cotton) must be corrected by deducting the amount of cellulose present in the organic trash. Similarly, organic trash contains inorganic materials, requiring a correction in the analysis for inorganics.

Filter Stripping

Samples for analysis of the three or four groups of contaminants are obtained from the pleated filters by air-stripping with a small funnel-shaped device (Figure 1) similar to an air-sampling filter funnel unit [4]. This unit is made of aluminum and a ceramic alundum disc * is placed inside as a filter. Flat rubber rings on each side of the disc are used as gaskets. The large-sized hypodermic needle (No. 14) on the inlet is used to traverse the top edges and the depressions of the filter. A needle with a side opening is attached to the funnel for traversing the

* Norton Company, porosity RA 98, 1½ in. in diameter and ⅛ in. thick.

TABLE I. RESULTS OF STRIPPING TESTS FOR ANALYSIS OF COTTON DUST COMPONENTS

Method of stripping	Filter No. 223* Sample (% ash)	Filter No. 223* Filter (% ash)	Filter No. 225* Sample (% ash)	Filter No. 225* Filter (% ash)	Filter No. 246 Sample (% ash)	Filter No. 246 Filter (% ash)	Filter No. 245 Sample (% ash)	Filter No. 245 Filter (% ash)
Stripping filter with No. 14 needle (Method 1)	28.7	—	27.5	1.75	49.3	1.66	45.6	2.32
Stripping filter with No. 14 needle and needle with side opening (Method 2)	32.2	—	31.1	1.38	49.0	1.44	46.0	1.64
Stripping cut and stretched-flat filter with No. 14 needle (Method 3)	28.7	—	29.9	1.40	48.8	1.40	48.2	1.51
Stripping cut and stretched-flat filter with large vacuum-cleaner unit	—	—	—	1.31	—	1.41	—	1.42
Total weight of sample on pleated filter (g.)	1.3300	—	0.4615	—	0.2925	—	0.5645	—
% Ash (Method 2) corrected for maximum error (see text)	33.6	—	34.6	—	54.6	—	48.7	—

* Samples collected on filters No. 223 and No. 225 were from the same source.

sides of the filter pleats. A small vacuum pump connected to the funnel nipple draws air through the unit when the needle inlet is placed against the pleated filter surface. The material removed is deposited on the alundum disc in the funnel. For each analysis, two opposite segments (pie-shaped) representing $\frac{1}{8}$ to $\frac{1}{4}$ of the filter area are stripped with both needles.

The sampling funnel, disc, and gaskets are weighed on an analytical balance to the nearest 0.1 mg. before and after stripping, the difference in weight representing the weight of the stripped sample. The unit is dismantled and the sample and disc are transferred to a beaker or crucible for the appropriate analysis.

Accuracy of determinations for inorganic dust, organic trash, and cellulose percentages is dependent upon the composition of the stripped sample when compared to the original sample from the pleated filter. Preliminary tests revealed that small amounts of the original sample remained on the filter after stripping. This unremoved material can create an error in the stripped sample if its composition differs from that of the original sample. The inorganic portion might exhibit greater imbedding power than either organic trash or cotton fibers because of smaller particle size and greater density. A stripped sample, therefore, may indicate a lower ash percentage and greater organic and cotton percentages than the original deposit on the filter.

Tests were made on four pleated filters containing typical cotton textile dusts collected in various yarn mill operations in order to determine this error and to make any corrections necessary for satisfactory results.

In the first tests ash determinations were made using three stripping methods on each filter to determine the desirable procedure. In some cases, ash determinations of the completely stripped pleated filter were made. The true ash content of the pleated cellulose filter was known; hence amounts of inorganics retained by the filter could be evaluated. The first method involved stripping the pleated filter with only the No. 14 needle. This technique appears satisfactory for the tops and bases of the pleats but unsatisfactory for the sides of the pleats since the needle opening cannot be placed flush against the filter surface.

In another method the No. 14 needle was used for the tops and bases and the other needle (with side opening) for the sides. The third method consisted of stripping the pleated filter after it had been cut and stretched out in a flat position with the No. 14 needle. By this procedure, the inlet to the needle can be placed flush with the filter surface at all times. Finally, a similar section of each filter was cleaned with a large vacuum cleaner unit, which is the best possible stripping method. (The large volume of air handled in this case did not permit collection of a sample and subsequent ash determinations.) The cleaned filter was then analyzed for percent ash to determine amounts of inorganic material retained under these optimum conditions.

The results of these tests are presented in Table I. The ash percentages determined by all three methods are in good agreement for each stripped filter. Stripping of the intact filter with only a No. 14 hypodermic needle leaves large amounts of inorganics. Visual observation of these sections revealed noticeable amounts of sample, including organics which were not removed by this method. The ash values obtained for filter sections cleaned by the other methods of stripping, including high-volume vacuum stripping, agree well. Since the known filter ash content

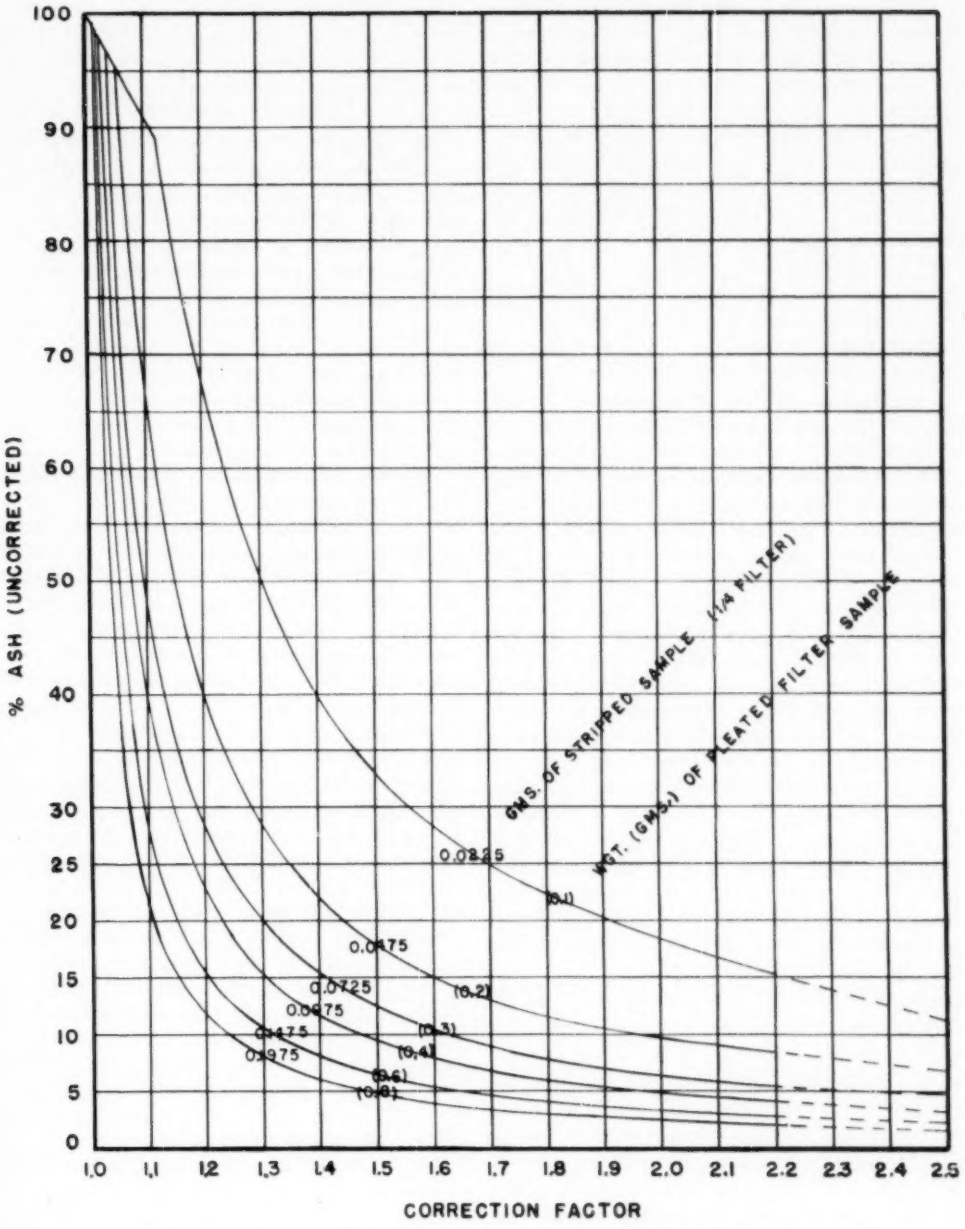

FIG. 2. *Correction factors (maximum error) for uncorrected ash percentage.*

is 1.200%, none of the methods used removed all of the deposited material.

The procedure employing both needles on the intact filter is preferable since the filter is not destroyed and is suitable for re-use after cleaning.

Although the ash percentages in the sample obtained with the different methods are in agreement, a significant error may result if the retained material is not of similar composition to that stripped. The magnitude of such an error is difficult (if not impossible) to determine. The maximum error, however, can be estimated by considering all possible sources of errors and their mathematical relationships. This information is important in interpreting the significance of the stripped-sample analyses.

The percentage difference between the filter-paper ash after stripping of a sample and the known ash content of new filters is approximately 0.25%. This value represents the inorganics not removed from the filter by stripping. If all of this amount of material is assumed to be inorganic, it represents the maximum error. Since the average weight of a clean pleated filter is 8.0 g., 0.25% is equivalent to 0.0200 g. of inorganics retained per pleated filter. The ash weight of a stripped sample would therefore be equal to the determined weight plus 0.0200 g. times the stripped fraction. This fraction is determined by the weight ratio of the stripped sample to the total material weight on the filter. In this determination it is assumed that the total air-borne sample was distributed uniformly over the pleated-filter surface. This assumption appears to be justified by the consistency of the ash percentages presented in Table I.

Stripping tests made on a clean unused filter showed that a small amount of cellulose fibers is removed by stripping. The average amount removed was 10 mg. per filter. Since the filter ash is only 1.2%, any filter-paper fibers removed were considered to be volatile and to add no significant amount of ash to the sample. The weight of sample obtained by stripping, however, must be corrected for this removed cellulose and the unremoved ash. The true weight of sample for a section of stripped filter, therefore, equals the determined weight plus the weight of the retained sample less the weight of the removed filter-paper fibers. The equation for determining the ash fraction as corrected for maximum error (assuming retained filter material to be only inorganic) is:

$$\text{Ash fraction (for maximum error)} = \frac{\text{ash wt.} + (0.0200)(\text{SFF}^*)}{\text{sample wt.} + (0.0200 - 0.0100)(\text{SFF})} = \frac{\text{ash wt.} + (0.0200)(\text{SFF})}{\text{sample wt.} + (0.0100)(\text{SFF})}$$

The material retained by the pleated filter probably contains some fine organic dust in addition to inorganic. The true ash percentage then has a value between the uncorrected amount and the ash percentage corrected for maximum error.

Although the ash value corrected for maximum error does not yield the true amount in the sample, it is important in determining the significance of the uncorrected ash value. The reliability of a determined ash percentage is indicated by the difference between the uncorrected values and the values corrected for maximum error. Results should include both values, as shown in Table I.

By using this correction method, it is possible to predict the sample size required for the desired accuracy. Calculations were made with different weights of samples containing various ash percentages obtained theoretically from stripping quarters of filters. Five mg. of ash were retained by the filter and 2.5 mg. of cellulose were added to the stripped sample weight. Uncorrected ash percentages were calculated and ratios of percent ash for maximum error to uncorrected percent determined for each case. This ratio, or correction factor, multiplied by the ash percentage uncorrected (determined) gives the maximum-error ash percentage. Figure 2 presents correction factors for ash percentage (maximum error) for many different stripped-sample weights. The weight values in parentheses represent total amounts collected by the pleated filter. For determination of ash in a given air sample with a desired maximum percentage error [% error = (correction factor − 1) × 100], the amount of sample required can be estimated if the approximate minimum ash in the air is known. For a maximum error of 10% with a minimum ash percentage in the air of about 40%, the amount of sample should be at least 0.400 g. The result obtained, however, should be corrected for by the above formula to give the uncorrected and corrected-for maximum-error ash values.

From the analytical results of many samples, the determined ash percentage (uncorrected) is believed to be closer to the true ash value than the percentage ash corrected for maximum error.

* Stripped filter fraction.

The organic trash and cellulose percentages are also subject to possible error from incomplete stripping. The magnitudes of these errors, however, are probably lesser, and certainly not greater, than those obtained from ash. The percentage of ash is the simplest and most accurate determination of the three components and its evaluation indicates the range of error for the others.

Correction for interferences and evaluation of all three components require analysis of two of the three components. Ash and either organic trash or cellulose determinations are always made on samples stripped from a given pleated filter for estimation of the components.

Analysis to Determine Components

Inorganic Dusts

This determination is based on the assumption that at ignition temperature for organic material the inorganic dust is non-volatile and equal to the ash weight. For the mineral dusts encountered in baled cotton, which contain only small amounts of carbonates and sulfides, this assumption does not introduce significant errors.

The weighed stripped sample collected on a preignited alundum disc, as described above, is placed in a pre-ignited Vycor crucible (50 ml.) with all the sample. A camel's-hair brush is used to transfer traces of material which adhere to the stripping funnel walls and gaskets. The crucible and its contents are weighed and the sample is ashed by conventional procedures. After cooling in a desiccator for 2 or more hours the crucible is reweighed. From these weights the percentage ash is computed.

Interferences.—Ash from cotton cellulose is less than 0.1% and is therefore negligible. Organic trash, however, contains appreciable ash, which amount must be deducted from the above determined total ash to give the correct percentage of inorganic dust in the sample. For the determinations reported here the ash in organic trash was obtained by ashing several representative samples of organic trash from machine-picked cotton which had been washed (decanted) several times with an inert solvent (CCl_4) to remove all inorganic dust particles. The ash percentage of such organic trash was approximately 10%. For practical purposes, therefore, the weighed ash value is corrected by deducting 10% of the weight of the organic trash in the pleated-filter sample. This correction requires evaluation of the fraction of organic trash in the original pleated-filter sample.

Organic Trash

Two procedures can be employed for the determination of organic trash in the stripped filter sample. One method is based upon the color formed when organic trash, principally leaf, is allowed to stand at room temperature (20° to 25°C) in 60% sulfuric acid (concentration by volume) for a period of 1 hr. The other method utilizes determination of nitrogen in trash by means of a microkjeldahl method.

Trash Color Method.—In determining cellulose directly, a procedure was developed which employs sulfuric acid as a solvent for the cellulose. When applying this procedure, it was observed that 60% sulfuric acid by volume gives complete solution without developing any reaction color from the cellulose unless heat is added or the sample stands for a considerable period. It was also noticed that raw cotton which contained organic trash when treated with 60% sulfuric acid (under the same conditions) developed a yellow-brown color in a short time. Tests indicated that this yellow-brown color was attributable not to the amount of cellulose contained in the organic trash but to compounds leached from the trash which perhaps reacted with sulfuric acid. The amount of color developed was found to increase significantly with smaller trash particles. Standard curves were prepared using particle-sized organic trash. When the particle size was < 325 mesh ($< 44\ \mu$), a reproducible curve was obtained. It was also observed that this color obeyed Beer's law. Maximum absorption occurs at a wave length of 410–420 mμ.

In order to use the trash color method as a quantitative procedure for leaf or organic trash in airborne samples, it is necessary to take bulk raw cotton samples from the process under study and hand-pick a large number of leaf and organic particles. These particles are then ground to pass a 325-mesh screen. A razor blade or sharp instrument can be used to cut fragments into small pieces. Most of the particles are dry and crush readily. A sample of this material can then be dried and weighed. As an alternative source, organic trash obtained from final leavings in pickers or other cleaning machines used for the cotton under investigation is suitable if cotton fibers are absent and if an ash determination of the < 325-mesh screened trash is made. The true

amount of organic trash in the sample is equal to the fraction volatile (1 − fraction ash) divided by 0.9, since 90% of organic trash is volatile. Trash from the latter source is preferred because it is more representative than trash from hand-picking, and the method is simpler and requires less time.

The following procedure was adopted for colorimetric determination:

1. A weighed sample is soaked in cold 60% sulfuric acid for 1 hr. and then filtered with suction through a dry, sintered-glass filter. The acid should be prepared at least 2 days before use since it apparently is not stable until the second day.

2. An aliquot, depending upon the color density, is made to 7 ml. volume with 60% acid, mixed, and read on a photoelectric colorimeter at a spectrum band of 410 to 420 mμ. We used the Coleman Model 11 Spectrophotometer or the Klett-Summerson colorimeter with a blue (No. 42) filter.

3. The amount of organic trash is determined from an appropriate standard curve prepared from weighed amounts of trash.

The maximum amount of sample that can be analyzed depends upon the amount of color produced by a given amount of the type of trash. With this method we found that 1.2 mg. of organic trash per ml. of 60% sulfuric acid produces maximum color scale in the Klett-Summerson colorimeter at 420 mμ. The sensitivity of the procedure is 20 to 40 μg. of leaf or organic trash per ml. of acid solution. The chief difficulty with the leaf-color procedure is that it requires a standard curve for each type of cotton used in the textile plant. Blended cottons may be used, however, within reasonable limits (± 5%) for determining organic trash in mill air samples.

In performing analyses from filter air samples, stripped material collected on the alundum disc is placed in a beaker and a measured amount (2–5 ml.) of 60% sulfuric acid is added. The solution is gently stirred until it is apparent that the surface of the filter is completely wetted, and then allowed to stand 1 hr. After filtering, an aliquot is made to 7 ml. with 60% sulfuric acid, as outlined above. The percentage of organic trash can be computed from colorimeter readings.

Interferences: Since cotton and inorganic dusts produce no color in cold 60% sulfuric acid for over a period of 1 day, no interference results. The influence of particle size and organic-trash color, however, makes the method only an approximate one.

Nitrogen Method.—The determination of organic trash by analysis of amino nitrogen is based upon the fact that cotton is principally cellulose and ordinarily contains negligible amounts of nitrogen, whereas leaf and organic trash contain a considerable proportion. We have found, however, that cleaned raw cotton may contain up to 0.175% nitrogen, with an average of 0.12%. Apparently this nitrogen is from the cell protoplasm. In analyzing cotton samples, the determination of trash by nitrogen evaluation may require large corrections because of the large amount of cellulose in relation to trash content. Where amounts of leaf and organic trash are a large percentage of the total sample, as in air samples, this error is insignificant. A satisfactory nitrogen method for this purpose is a modified microkjeldahl analysis. The trash sample is oxidized in boiling concentrated sulfuric acid to which a few drops of hydrogen peroxide have been added. The amino compounds are converted to ammonia, which is determined colorimetrically by means of Nessler's reagent. This is an extremely sensitive colorimetric procedure and small amounts of amino nitrogen are easily determined. Amounts as small as 1 μg. per 7 ml. of solution can be determined with the Klett colorimeter.

The nitrogen method for air analysis is as follows:

Take a stripped sample with an alundum filter disc as for ash determinations and obtain its stripped weight. The disc and collected sample are placed in a beaker and exactly 5 ml. of concentrated sulfuric acid are added. The beaker is heated gently to dissolve the sample and a few drops of 30% H_2O_2 are then added to clear the solution. Clearing is necessary in order to observe when the sample is completely dissolved. The digestion is continued and more peroxide is added if necessary until complete solution is obtained. After cooling, pipet 1 ml.* into a 30-ml. pyrex test tube. Apply heat slowly with a microburner until dense white fumes appear. This solution will be deeply colored. Allow the tube to cool for about 20 sec. and add 30% hydrogen peroxide, dropwise, until the solution becomes clear and colorless. If color returns, repeat the oxidation until the solution is again clear. Cover the test tube with a watch glass and boil gently for 2 to 5 min. Allow the tube to cool and transfer the contents into a

* The error introduced by neglecting the change in volume of solution caused by peroxide addition is negligible unless more than 5 or 6 drops have been added. Usually 5 drops are sufficient. A larger aliquot may be taken, but final acid concentration should be close to that in the standards.

100-ml. standard volumetric flask. Dilute to 100 ml. with water, part of which has been used to rinse out the digestion tube, and mix well. Pipet 5 ml. into a colorimeter tube, and add 2 ml. of Nessler's reagent. Shake and measure on a colorimeter against a blank containing 5 ml. of distilled water and 2 ml. of Nessler's reagent. In the Klett-Summerson colorimeter a blue No. 42 filter with a range of 400–440 mμ is used. A value (10 in this case) is deducted from the colorimeter reading and the nitrogen is then determined from a standard curve. The net reading is based on the value obtained from a digested blank. This deduction should be checked when new reagents are used. An arithmetical deduction from the reading is permissible since the color obeys Beer's law and the Klett colorimeter scale is logarithmic. We have found it convenient to use prepared Nessler's salt obtained from scientific supply houses.

Since a total aliquot of $(1/20)(1/5) = 1/100$ is used for analysis, the nitrogen in the disc sample is 100 times that in the aliquot. Larger aliquots and smaller dilutions can be used to increase the sensitivity. For sample weights necessary to minimize the possible stripping error, the suggested aliquots and dilutions are satisfactory for the usual amounts of nitrogen.

The organic trash in the sample is ten times the nitrogen percentage, since it contains approximately 10% of nitrogen. This value in organic trash varies with the type and possibly the age of the cotton and with the composition of the organic trash. The trash components are also variable, since they contain various percentages of leaf, seed fragments, stems, and other materials. Nitrogen in picker trash averages 5 to 6%, but this includes many ingredients not ordinarily air-borne. Air samples contain more than 6% of N (one had 8%), indicating that air-borne organic trash contains a higher percentage of N than picker material does. When a value of 10% N in organic trash is used for computation, results are in agreement with analyses for other constituents.

Nitrogen analysis for organic trash is preferable to the color procedure using 60% sulfuric acid. Results are more consistent and the method is simpler. We have observed in field research that there is a relationship between the amount of organic trash in air and the incidence and the severity of cotton mill fever. Some investigators believe that this disease is caused by a foreign protein. If this hypothesis is correct, then amino nitrogen may be involved.

Both trash evaluation methods have the same limitations with respect to variabilities in type and composition of organic trash. Nitrogen analyses, however, are not influenced by particle-size factors.

Interferences: Significant interference is present only in air samples of low organic-trash content where there is nitrogen from cotton-fiber cell protoplasm. This occurs when amounts of air-borne lint are appreciable, as shown below with low organic-trash and inorganic-dust contents. In such cases, approximate corrections can be made which will indicate the accuracy of the results. Since approximately 10% of ash is present in organic trash and 0.12% of nitrogen in the clean cotton fibers, then:

Let X = organic-trash fraction in sample;
Y = cotton fraction in sample;
Z = inorganic fraction in sample;
N = nitrogen fraction in sample;
A = ash fraction in sample.

And, as constants:
0.1 = nitrogen fraction in organic trash;
0.0012 = nitrogen fraction in clean raw cotton;
0.1 = ash fraction in organic trash.

From these assumptions we can establish the following relationships:

$$A - 0.1\,X = Z \text{ (ash in cotton negligible);} \quad (1)$$

$$1 - X - Z = Y \text{ (entire sample divided into these three components);} \quad (2)$$

or, by substituting equation (1) in equation (2):

$$1 - 0.9\,X - A = Y. \quad (3)$$

For nitrogen analyses:

$$(0.1)(X) + (0.0012)(Y) = \text{fraction nitrogen in sample } (N). \quad (4)$$

Substituting equation (3) in equation (4),

$$X = \frac{N - 0.0012(1 - A)}{0.0989}.$$

High ash fractions (0.05 to 0.40) occur only with high nitrogen values in the sample (0.01 to 0.08). In these cases the percentage error introduced by neglecting the formula is small. For example, 2% nitrogen and 20% ash would give 0.1925 as the fraction of organic trash (19.25%) by the formula and 0.2000 if 10% nitrogen in trash is used alone. This results in a difference of 3.9%. Small nitrogen values in air samples are accompanied by low ash

fractions and the error introduced by neglecting the formula in these cases can be appreciable. For example, 0.5% N and 2% ash would give 3.8% organic trash by the formula and 5% using 10% N alone as an index (29% error).

Calculation of the organic trash formula may be in error if the cell nitrogen deviates widely from the 0.12% average. The error from this source is considerably less than that resulting from disregarding the formula. It must be noted that 10% nitrogen in organic trash is only an approximate value. Consideration of all sources of error are important in interpreting the analytical results.

Cotton

The third important component of atmospheric dust in cotton textile plants is short cotton fibers. Analysis for cotton is based on determination for cellulose, since this material is the chief component (< 0.1% ash, 0.08–0.175% N). Two methods have been developed for the determination of cellulose. One utilizes color produced on heating a sulfuric acid-cellulose solution (acid color method) and the other employs a reagent known as anthrone.

Acid Color Method.—Cellulose dissolves in 60% (by volume) sulfuric acid and gives a colorless and almost clear solution. On heating aliquots of this solution with concentrated sulfuric acid for a known period in boiling water, a brown color develops. The color depth is proportional to the amount of cellulose and also obeys Beer's law. Conditions of the reaction such as quantities of concentrated acid, time of solution, and heating have been studied for optimum conditions. The following procedure was developed:

A stripped sample on an alundum disc obtained from a pleated-filter sample is placed in a beaker. A quantity of 60% sulfuric acid, the amount depending upon the sample size and estimated amount of cellulose, is placed in the beaker and allowed to stand for from 15 min. to 1 hr.* The amount of 60% acid should be such that a 2.0-ml. aliquot contains 0.02–0.5 mg. of cellulose. The alundum disc should be covered with solution, and after the dissolving period the sample is filtered through a dry Gooch asbestos or sintered-glass filter with suction. Five ml. of concentrated sulfuric acid are added to a 2-ml. aliquot in a test tube and mixed. This solution is heated in a boiling-water bath for 55 ± 5 min. and cooled for 20 to 30 min. in cold water. The color of the solution is read at 410 to 420 mμ (Klett colorimeter—No. 42 filter). The amount of cellulose in the aliquot is ascertained from a standard curve prepared from known amounts of cellulose in 2-ml. aliquots. It is important to note that standards and samples must not be diluted and aliquots consistent with the standard curve should be used.

Interferences: Obviously, materials other than cotton which contain cellulose will interfere. In addition, materials which dissolve in 60% sulfuric acid and cause color formation on standing 1 hr. to 2 hrs. or on addition of concentrated acid and heating will also interfere. Such interference results from cellulose in organic trash and acid-soluble substances causing the formation of color. Correction for this error is approximate and can be done only when the amount or the percent of organic trash in the sample is known. Cellulose analysis by this method on cotton-free organic trash yielded values from 30% to 38% (mean, 34%) for particle-sized trash (< 325, 200–325, 30–40 meshes). The cellulose determined from the cotton in the sample is corrected by the 34% factor.

The standard curve is prepared by dissolving known amounts of cotton in 60% sulfuric acid and allowing them to stand for 1 hr. The amounts of cotton dissolved are dependent upon the acid volume and the desired standard curve concentrations. A range of 0 to 0.5 mg. per 2-ml. aliquot was satisfactory. Two-ml. aliquots of each standard cotton-acid solution are added to 5 ml. of concentrated sulfuric acid, as described for sample analysis. Standards prepared from different-size aliquots of cotton dissolved in 60% acid but with the same acid concentration in the final solution gave inconsistent results. Results were uniform and obeyed Beer's law only when the same volume of aliquot was used. For this reason, 2-ml. aliquots are suggested for both samples and standards.

Anthrone Method.—This method depends on the reaction of concentrated sulfuric acid-anthrone reagent with an aqueous solution (or suspension) of a carbohydrate. A green color develops which under controlled conditions obeys Beer's law and its depth is proportional to the amount of carbohydrate present. This reagent is specific for carbohydrates and has been used for sucrose, starch, and cellulose analyses.

* If an analysis for organic trash by the sulfuric acid color method is to be performed on the same solution, it should stand for 1 hr.; otherwise, 15 to 30 min. is sufficient.

This procedure for cellulose and starch is detailed elsewhere [8], but details are presented here to expedite analyses. The stripped sample is digested (cold) for 15 to 30 min. in 60% sulfuric acid. There should be enough acid to cover the alundum disc and contain 10–200 μg. of cellulose in a 0.5-ml. aliquot. If a residue appears, it is filtered through a dry asbestos mat which has been washed with 60% sulfuric acid and water. A 0.5-ml. aliquot is then added to 2.0 ml. of water and the solution is allowed to cool. Four ml. of a 0.1% anthrone solution in concentrated sulfuric acid (4 hrs. to 9 days old) is added rapidly from a pipet or buret. The solution is mixed immediately and allowed to cool in air. After 10 to 15 min., the tube is cooled in cold water. A reference blank containing 2.0 ml. of distilled water, 0.5 ml. of 60% sulfuric acid, and 4.0 ml. of 0.1% anthrone reagent is treated similarly. Standards are prepared from 0.5-ml. aliquots of known amounts of cellulose in 60% sulfuric acid and treated similarly. The samples are read on a photoelectric colorimeter at 625 mμ. From these readings and a standard curve, cellulose concentrations are determined.

Since anthrone reagent exhibits changing sensitivity on standing any length of time, one or more standards must be prepared for each group of analyses to determine the slope of the standard curve which follows Beer's law. Beer's law is obeyed for anthrone solutions 4 hrs. to 9 days old. The heat of mixing of concentrated sulfuric acid and the carbohydrate solution or suspension is a necessary factor in the reaction. The cooling technique described above gives consistent results.

Interferences: Carbohydrates soluble in 60% sulfuric acid will interfere. These include cellulose and possibly other carbohydrates contained in organic trash or, in the case of weaving-room air samples, starch from sizing materials.

Starch can be removed by aqueous extraction (boiling with distilled water and filtering through a sintered-glass or an asbestos filter). The filtrate can be used for starch analysis. The filter residue can be analyzed for cotton by digesting it for 15 to 30 min. in cold 60% sulfuric acid and refiltering to remove asbestos fibers and other insoluble material.

Interference from carbohydrates of organic trash can be evaluated by utilizing trash analysis for cellulose. The amount of organic trash and its percent cellulose content should be known. Cellulose in inorganic trash determined by the anthrone procedure showed values of 20% to 21.9% (mean, 20.6%) for the particle sizes studied (< 325, 200–325, 30–40 meshes). The value for cellulose determined by analysis is therefore corrected by using the 20.6% value.

The anthrone procedure is preferable to the sulfuric acid color method because of its greater consistency and accuracy. Correction for organic-trash interference is subject to smaller error because of relatively constant amounts of cellulose in organic trash determined by the anthrone procedure. Interferences in the anthrone procedure are considerably less than those present in the acid color method.

Starch

The starch-analysis method is similar to the cellulose-anthrone method. Since starch is usually accompanied by cotton linters, a separation must be made. (Testing of weaving-room air samples requires this additional procedure.)

The stripped sample and disc are boiled in distilled water to dissolve starch (cellulose, which is insoluble, remains undissolved). After cooling, the solution is filtered through a fine-pore sintered-glass or asbestos filter. More water is added to the beaker containing the disc, and the liquid is again boiled and filtered. This step is repeated until all the starch is present in the filtrate. The residue is then digested with 60% acid and analyzed for cellulose. The filtrate is made to known volumes with distilled water. The final volume should be adjusted so that a 2.0-ml. aliquot contains 10–200 μg. of starch. This aliquot is treated with 4.0 ml. of 0.1% anthrone-sulfuric acid reagent (4 hrs. to 9 days old) added rapidly from a pipet or buret. The solution is mixed immediately and allowed to air-cool. After 10–15 min., the tube is cooled in cold water. A reference blank containing 2.0 ml. of distilled water is treated similarly. At the same time one or more 2.0-ml. starch standards (100 μg. is suitable) are also treated. Samples and standards are read at 625 mμ in a photoelectric colorimeter, as in the case of cellulose determinations.

Interferences.—Cotton interferes, but it would have been removed by the initial separation. (Cotton contains approximately 1% of water-soluble carbohydrates.) Interferences from leaf or organic trash are not significant since weaving-room air samples contain only clean cotton fibers and slight traces of organic trash. Water-soluble carbohydrates from the small amount of organic trash potentially present

TABLE II. METHODS FOR ANALYZING COTTON CONTAMINANTS IN AIR

Contaminant	Method	Interference
Inorganic dusts	Ash determination	Ash in organic trash
Organic trash	Direct color with 60% H_2SO_4	None
Organic trash	Nitrogen determination	Nitrogen in cotton fiber in samples of high cotton content (>90%)
Cotton	Sulfuric acid color method	Color contributed by organic trash
Cotton	Cellulose determination with anthrone	Carbohydrates from organic trash
Starch	Starch determination with anthrone	None

would be very small. (Organic trash contains approximately 3% of hot-water-soluble carbohydrates, based upon the anthrone reaction.)

Table II presents in outline form the methods of analysis and their interferences which have been discussed above.

Evaluation of the Components of Air Contaminants

Starch is present only in weaving-room air samples and no interferences exist. Cellulose determinations in these samples are free from interferences, since organic-trash contamination is absent or negligible. Air samples taken at the other yarn-mill operations preceding weaving (except sizing operations, where air samples are unnecessary) do not involve starch; hence only the other three contaminants are considered.

Analysis for inorganic dusts (ash) is the simplest and most accurate method for evaluating the components of air samples from pleated filters. Analysis for one other component (organic trash, or cotton) permits evaluation of all three, since the third may be determined by difference.

The choice of the other contaminant to analyze in addition to inorganic dusts and of the method of analysis is governed by certain factors. Obviously, selection of a method in which no interferences would be encountered would be best. However, analysis for organic trash by color in 60% sulfuric acid is the only one without interferences. But this method gives low accuracy because of particle-size influence and variations in the type and the composition of organic trash. If analysis for organic trash is desired, nitrogen determination has proved to be the most satisfactory. Where the amount of organic trash is presumed to be high, analysis for cotton is preferable since greater over-all accuracy can be obtained. If both analyses give the same percent accuracy, determination of the component comprising the smaller percentage permits greater precision in determining the other component if it is obtained by difference. For analysis of cotton, the anthrone procedure is the most satisfactory. Interferences encountered with this method can be more accurately corrected for than those of the acid color method. If possible, analysis for all three components is recommended as a check procedure.

The values for the components determined by the analyses (ash, nitrogen, cellulose percentages) are calculated from formulas, as follows:

Using the symbols and values given above for nitrogen-interference corrections and adding

Ce = fraction cellulose in sample

and

0.21 = fraction cellulose in organic trash (anthrone procedure),

the following equations are obtained:

$$Z + 0.1\,X = A \quad \text{(all ash from inorganic dusts and organic trash)}; \tag{1}$$

$$X + Y + Z = 1 \quad \text{(three-component sample)}; \tag{2}$$

$$0.1\,X + 0.0012\,Y = N \quad \text{(all nitrogen in organic trash and cotton)}; \tag{4}$$

$$Y + 0.21\,X = Ce \quad \text{(all cellulose in cotton and organic trash)}. \tag{5}$$

If analyses for ash and nitrogen are made, then

$$Z = A - 0.1\,X; \tag{3}$$

$$Y = 1 - A - 0.9\,X;$$

$$N = 0.0989\,X + 0.0012\,(1 - A).$$

Solving for the components:

$$\text{(Organic trash)}\quad X = 10.11\,N - 0.012 + 0.012\,A;$$

$$\text{(Inorganics)}\quad Z = 0.999\,A + .0012 - 1.01\,N;$$

$$\text{(Cotton)}\quad Y = 1.011 - 1.011\,A - 9.10\,N.$$

Fractions of organic trash, cotton, and inorganic dust can be evaluated from the above formulas from ash and nitrogen analyses. If analyses for ash and cellulose are made, then, by solving for the components:

$$\text{(Cotton)}\quad Y = Ce - 0.304\,(1 - Ce - A);$$

$$\text{(Inorganics)}\quad Z = A - 0.145\,(1 - A - Ce);$$

$$\text{(Organic trash)}\quad X = 1.449\,(1 - A - Ce).$$

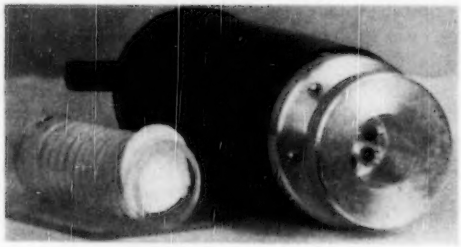

FIG. 3. *Hand sampling pump and alundum filters.*

Organic trash, cotton, and inorganic dusts can be evaluated by the above formulas from ash and cellulose analyses.

It is suggested that analysis for three components (ash, nitrogen, and cellulose) be performed occasionally and that the contaminants be evaluated by both sets of formulas. In this way, changes in formula constants may be revealed by discrepancies between the two methods. Such discrepancies can then be corrected by determining correct constants for the cotton being processed. Important constants are those for percentages of nitrogen, ash, and cellulose in organic trash. The ash and cellulose are apparently fairly constant in most cases and variations in nitrogen are probably responsible for any discrepancies. The correct nitrogen value may be obtained indirectly from the total composition by ash and cellulose analysis.

Accuracy of results is best indicated by analysis for the three constituents (ash, cellulose, and nitrogen). Significance of the results can be determined by considering the stripping errors discussed previously.

Inefficiency in filter stripping is responsible for errors in ash determination and also produces errors in evaluation of the other contaminants. The inorganic material retained by the pleated filter reduces its calculated percentage and increases organic trash and cotton values in the stripped sample. Percentages of cotton and organic trash from stripped-sample analyses are therefore higher than those present in the original pleated-filter sample. Exact evaluation of these fractions is difficult, and not possible by the methods described above. Determination of maximum error, however, as in ash determinations, permits interpretation of the significance of the values obtained for fractions of cotton and organic trash.

Maximum error is based on the assumption that all filter material retained is inorganic. It was shown that some filter cellulose was removed by stripping and represents part of the removed sample. This collected sample, therefore, is low in ash, creating increases in organic trash and cotton. Because of the filter cellulose removed, the determined "cotton" in the sample is increased additionally. Data presented above show that 0.0200 g. of ash can be retained on the pleated filter while 0.0100 g. of cellulose on the filter may be removed by stripping. The sample weight corrected for maximum error equals the actual weight plus retained inorganics less cellulose fibers removed; *viz.*:

$$\text{Sample weight} + (0.0200 - 0.0100) \text{ stripped filter fraction (SFF)}.$$

Weights of sample components corrected for maximum error can be arrived at similarly:

$$\text{Inorganic fraction} = \frac{\text{inorganic wt.} + 0.0200\ (\text{SFF})}{\text{sample wt.} + 0.01\ (\text{SFF})}.$$

$$\text{Organic trash fraction} = \frac{\text{organic trash wt.}}{\text{sample wt.} + 0.01\ (\text{SFF})}.$$

$$\text{Cotton fraction} = \frac{\text{cotton wt.} - 0.01\ (\text{SFF})}{\text{sample wt.} + 0.01\ (\text{SFF})}.$$

In order to determine the fraction components for maximum error, it is necessary to know the weight of the sample, of the stripped filter fraction (SFF), and of the components. The sample weight is known from analysis of the components. The stripped filter fraction is equal to the sample weight divided by the pleated-filter sample weight. The weight of the components is determined from the uncorrected fraction and the total sample weight. The third component is corrected for maximum error by difference.

The composition analyses of atmospheric contaminants should include uncorrected values and results corrected for maximum error. From this information, the significance of the results can be seen.

Sampling for Specific Air-Borne Components

Sampling for specific components in air can be made directly when dust concentrations are high. Air collection is made by a hand pump (600 ml. per stroke) modified from the welding fume sampler described by Silverman and Ege [5]. This apparatus, shown in Figure 3, was modified by placing a rubber-flap check valve in the inlet and providing a holder

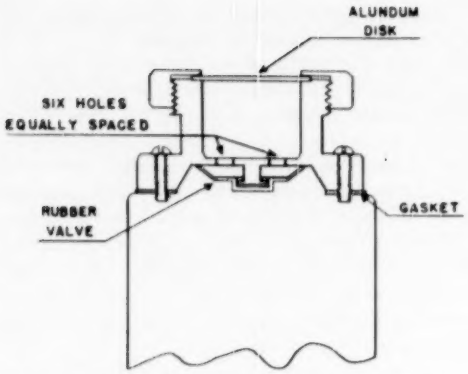

FIG. 4. *Cross section of modified sampling head for alundum filters.*

in which an alundum disc (described previously) is placed. The sampling-head changes necessary for textile dusts are shown in detail in Figure 4. The check valve prevents reverse air flow through the low-resistance alundum disc. Alundum is a chemically inert material and the collected sample can be analyzed by chemical methods.

Air sampling with the hand-pump technique is adapted to mill conditions where the contaminants are primarily cellulose and starch. These may be determined by methods described above. Organic-trash determinations are obtained with sufficient accuracy by this method, using the nitrogen method of analysis. Determinations of inorganic materials by ash analyses and determination of cotton by cellulose are only approximate. The Lucite sample holder shown in Figure 3 is used for carrying clean discs into the field, and small aluminum weighing dishes with covers are used for collected samples.

Summary

The nature of air-borne contamination encountered in cotton textile mills is described and classified into three components: inorganic material, organic trash, and cotton. Starch particles from sizing materials constitute a fourth component in weaving-room air samples.

Air samples are collected on a pleated cellulose filter at a high sampling rate (70 cu. ft./min.) permitting short sampling periods and gravimetric analysis for total contamination. Representative samples for analysis of components are obtained from the filter sample by means of air stripping. The stripping technique is fully described, including stripping errors and their significance in the results.

Chemical determinations and the evaluation of the above components are presented. A discussion of the advantages and disadvantages of the methods cited and their interferences are included.

Grab sampling for specific components is also discussed.

Acknowledgment

We are indebted to the Saco-Lowell Shops and the Nashua Manufacturing Company, whose gift to the Harvard School of Public Health made this work possible.

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Water-Impermeable, Water-Vapor-Permeable Coated Fabrics

Development of a Waterproof Coated Fabric Which Transmits Body Perspiration*

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Introduction

The limitations of rubberized coated fabrics, plastic films, or plastic-coated fabrics for use in rainwear apparel have long been recognized. While such materials afford effective protection from the rain, their very limited ability to transmit body perspiration away from the wearer results in the problem of heat build-up on the inside of the impermeable garment, with resultant sweating and chilling.

The following discussion deals with the research work and the laboratory and field testing involved in the development of a coated fabric to meet the need for a water-impermeable, water-vapor-permeable fabric.

Background

Exploratory studies by C. L. Woodworth [5] at the Quartermaster Climatic Research Laboratory, Lawrence, Mass., were carried on to determine the limits of water-vapor permeability necessary in a fabric for comfort. His work showed that in order for a water-impermeable, water-vapor-permeable fabric to be practical, its ability to transmit moisture vapor would have to approach closely that of an uncoated fabric. As a result, the first attempts to produce a water-impermeable, water-vapor-permeable fabric centered around the improvement of the water-resistance of the various water-repellent-treated fabrics. Extensive work showed this line of attack to be difficult. While excellent moisture-vapor transmission rates could be obtained with this type of treatment, no successful method could be found to develop a hydrostatic head of 75 cm. of water at the same time. This hydrostatic head, held for 5 min. on the Suter Hydrostatic Head Tester, is the minimum requirement for waterproofness.

Having exhausted the possibilities in the above line of attack, the next approach seemed to be to develop in the waterproof rubberized coatings the property of moisture-vapor transmission. It was immediately recognized that in order to achieve this end it would be necessary to incorporate into the coating channels which would transmit moisture vapor. To accomplish this without destroying the waterproofness presented a most difficult problem. Mechanical or electrostatic perforation of the coated fabric destroyed the waterproofness, while improving only slightly the fabric's ability to transmit moisture vapor.

The first method developed as a means of transmitting moisture vapor through a rubberized fabric was the incorporation into a rubber matrix of porous pigment in such a manner that the pigment particles would touch each other. This would allow moisture-vapor transmission through the coating from particle to particle of the pigment. In further development of this theory, a number of porous pigments were studied. Consideration was given to such properties as low density, low thermal conductivity, fireproofness, and mildew-resistance. The porous pigment finally selected had all of the above properties but was highly hydrophilic. Since it was planned to use a rubber latex as a binder, it was known that this highly hydrophilic pigment would coagulate the latex. In addition, a hydrophilic pigment in an open coating would absorb relatively large quantities of water. Therefore, the pigment was subjected to a silicone treatment, making it hydrophobic, and this treated pigment was then incorporated in the rubber latex. Coated fabrics were produced on a tenter-frame

* The opinions expressed herein are those of the authors and are not to be construed as the official view of the Quartermaster Corps or the Department of the Army.

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spreader and showed some measure of moisture-vapor transmission.

Attempts were made to measure the air permeability of these moisture-vapor-permeable fabrics [1]. The values obtained were below the lower limits of such conventional apparatus as the Gurley Densometer or the Frazier Permeameter. Because relatively high rates of moisture-vapor transfer had been obtained on these fabrics, it was concluded that there was no relationship between air permeability and moisture-vapor permeability for this type of fabric.

The development of a water-impermeable, water-vapor-permeable fabric having shown some promise, a research contract was let to the Chemical Products Development Division of The Goodyear Tire & Rubber Company.

After experiments with various latices and production procedures, coated fabrics were produced on large-scale equipment, using the silicone-treated porous pigment and a synthetic rubber latex. Since these coated fabrics had relatively low rates of moisture-vapor transfer when compared to uncoated fabrics, it was deemed necessary to conduct comfort tests to determine whether further work was warranted. Garments were constructed and sent to the University of Indiana for testing.

During these tests, conducted by S. D. Gerking and Sid Robinson [4], Department of Physiology, Indiana University Medical School, to determine the heat stress imposed by impermeable, wet-weather suits and the experimental water-impermeable, water-vapor-permeable suits, comparison was made of the relative coolness of the following 4 types of clothing: (1) poplin jungle uniform; (2) wet-weather suit with permeable coating; (3) wet-weather suit laminated with permeable coating; (4) impermeable wet-weather suit. All of the wet-weather garments were made in the same design.

The experiments were performed on men walking on a treadmill at a metabolic rate of 190 cal./m.^{2} per hr. The subjects used in the tests were all well acclimatized to the heat and maintained water balance during the 2-hr. experiments by drinking measured quantities of 0.1% salt solution. The wet-weather suits were worn by the men in 4 different environments: air temperature 17.4°C, with 57% R.H.; 24.1°C, 50% R.H.; 30.5°C, 80% R.H.; and 37.9°C, 29% R.H. The last environment was used to determine the maximum rate at which sweat could be evaporated from the clothing. In addition to the suits, the subjects wore shorts, shoes, and socks in each experiment.

In all of the 2-hr. experiments, the weights of the men, both clothed and nude, were determined hourly in order to follow their rates of sweating and evaporation. The skin temperature of the men was taken at 15-min. intervals by 4 thermocouples placed separately on hip, chest, shoulder, and knee. Rectal temperatures were taken every half-hour with a clinical thermometer, and heart rates were recorded at 15-min. intervals by an electrocardiotachometer.

At air temperatures of 24.1°C and 30.5°C, the comparisons of the clothing consisted of 2 experiments in which 2 men walked on the treadmill simultaneously. In these studies, each subject wore each type of test garment. The data for both men for each type of garment were averaged to offset variations in the environment and the performance of the men from day to day. At 17.4°C and 37.9°C, 4 subjects wore 4 different types of clothing in only one experiment each; thus, no direct comparison of the garments was obtained in these environments.

The water-impermeable, water-vapor-permeable suits had a distinct advantage in a hot, dry environment (37.9°C, 29% R.H.), where a high rate of evaporation was required. The subject who wore the impermeable suit under these conditions was barely able to complete 1 hr. of work, while the subject who wore the water-impermeable, water-vapor-permeable suit was not taxed to complete 2 hrs. of the same work. Based on the rates of sweating, skin temperatures, rectal temperatures, percent of sweat evaporated, and heart rates of the men in all environments, the clothing was classified as to relative coolness in the following order: (1) poplin jungle uniform; (2) wet-weather suit with permeable coating outside; (3) wet-weather suit laminated with permeable coating; (4) impermeable wet-weather suit.

These tests on water-impermeable, moisture-vapor-permeable fabrics conclusively proved that the moisture-vapor transmission rate was sufficiently great for the fabric to be of practical value for specific application.

While the treated porous pigment-synthetic rubber latex combination did result in a coated fabric which was water-impermeable and water-vapor-permeable, as shown by laboratory and comfort testing, the coating itself had many features which were objectionable from a processing and physical-property standpoint.

TABLE I. COMPARISON OF WATER-IMPERMEABLE, WATER-VAPOR-PERMEABLE FABRICS WITH RUBBERIZED AND WATER-REPELLENT FABRICS

Fabric	Moisture-vapor transmission (% of that transmitted by base fabric)	Hydrostatic head (cm. water) ASTM test*	Suter test†
Water-repellent fabric	100		10–50
Rubberized fabric	0–10	300+	278+
Fabric coated with porous pigment-latex binder	25	200	
Fabric coated with untreated porous pigment-latex binder	42	250	
Fabric coated with untreated porous pigment-solvent cement binder	58	250	
Fabric coated with solid pigment-solvent cement binder	73	300+	278+

* Fifth drop through a 3.12 in.² area.
† First drop through a 15.9 in.² area.

Because the basic spreading material was a water dispersion, difficulties were encountered with drying, shrinkage of fabrics, and corrosion of equipment. In addition to being costly and difficult to control, the coating was of an extremely weak nature. Extensive work resulted in limited progress in overcoming these difficulties. It became evident that new approaches would have to be investigated.

Concentrated effort soon brought forth a number of entirely new concepts on the problem. A naturally occurring porous pigment was found which could be successfully used without the necessity of a water-repellent treatment. Since the solubility of the silicone treatment had previously limited the binders to latices, this finding presented the possibility of the use of solvent rubber cements as binders. This meant that not only could the costly treatment be eliminated, but the coating material would lend itself to conventional rubber spreaders.

The porous pigment-rubber cement combination was successfully reduced to practice. Coated fabrics which had excellent properties when compared with those of the treated pigment-rubber latex type were produced on large-scale equipment. While this coating was a marked improvement over the previous product, a number of necessary properties were still lacking. The coating lacked the required strength, it possessed less than satisfactory ageing characteristics as measured on the Weatherometer, and it failed to withstand washing and/or dry-cleaning.

During the course of these investigations, experiments were undertaken using a solid pigment with a rubber cement, and it was discovered that a water-impermeable, water-vapor-permeable fabric could be made with this combination. It was eventually demonstrated that this coating functioned by means of a complicated, three-dimensional, interconnected structure of micropores. Since this last approach had produced a coated fabric which had the most reproducible and the most satisfactory physical properties of the various coatings tried, its theory will be considered in more detail. It was work on this concept which finally produced the coated fabric which was presently developed to a usable stage.

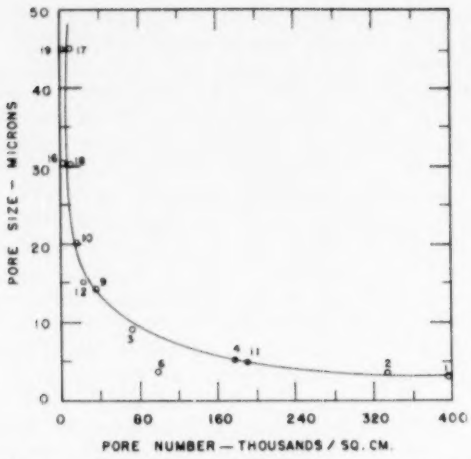
While the early stages of this development have been discussed somewhat briefly, they do represent tremendous strides toward the development of a water-impermeable, water-vapor-permeable fabric. This can be clearly seen upon examination of the data in Table I.

Discussion

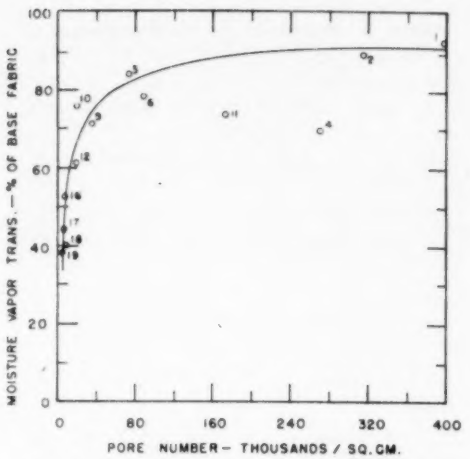
Theory

In order to obtain a porous coating using a solid pigment and rubber, an entirely different approach was used from that which has been normally recognized in this field. Using a solid pigment means that the pores have to be developed *around* the pigment in the coating upon drying. It is a known fact that, because of their particle size and shape, pigments occupy much larger volumes than their true specific gravity indicates. This is true even under wetted, centrifuged conditions and suggests that there is some void space between the pigment particles. If it is possible to add rubber to the pigment in such volume that it will bind the pigment particles together without occupying all of the void space available between the wetted packed particles, then it is possible to produce pores with the remaining void space upon drying the coating.

This theory might be more easily understood by considering an example: 100 g. of a pigment having a specific gravity of 2.70 were found to occupy 127 cc. under wetted, centrifuged conditions. Based upon its true specific gravity, 100 g. of this pigment should occupy only 37 cc. This would mean that 90 cc. of void space occurs between the pigment particles; this space would be available for binder and pores. If 50 cc. of binder were used to bind together



GRAPH 1. *Plot of the number of pores* vs. *pore size for a number of different fabric coatings.*



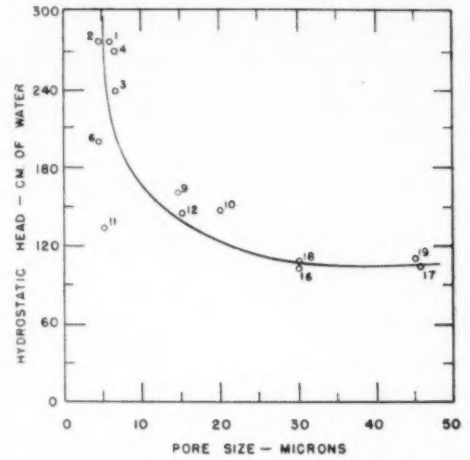
GRAPH 2. *Plot of the number of pores* vs. *moisture-vapor transmission for a number of different fabric coatings.*

the 100 g. of pigment, then there would be 40 cc. of void space in the coating. On a percentage basis, this would mean that 31.5% of the coating would be made up of voids.

A large number of pigments were examined under wetted, centrifuged conditions. In some pigments, the available void space was considerably larger than in others. In fact, various grades of the same pigment were found to have extreme variation in the void space available. Knowing this, and considering the above theory, it could be seen that the pigment particle size and particle shape greatly influence both the number and the size of the pores developed.

It could then be visualized that a given volume of void space could be accomplished either by the production of a large number of small pores or by the production of a small number of large pores, depending upon the choice of the pigment. Producing and studying actual coatings was the only way to determine whether or not this was true.

A large number of pigments and rubber binders were tried in various ratios of pigment to binder. These blends were coated upon a base fabric, and some of the resulting coatings were studied under a microscope. Graph 1, which is a plot of the number of pores *vs.* pore size, is the result of surface microscopic examination of these coated fabrics. It will be noted from the curve that in this type of coating, as theorized, the number of pores per sq. cm. increases as the size of the pores decreases. Having established the existence of a wide variation of pore size and number within the sample coatings, it was most interesting to study the moisture-vapor transfer and hydrostatic-head resistance of these same coatings. Graph 2, which is a plot of the number of pores *vs.* moisture-vapor transmission, indicates that moisture-vapor transfer takes place as long as a sufficient volume of pores is present, whether the



GRAPH 3. *Plot of the pore size* vs. *hydrostatic-head resistance for a number of different fabric coatings.*

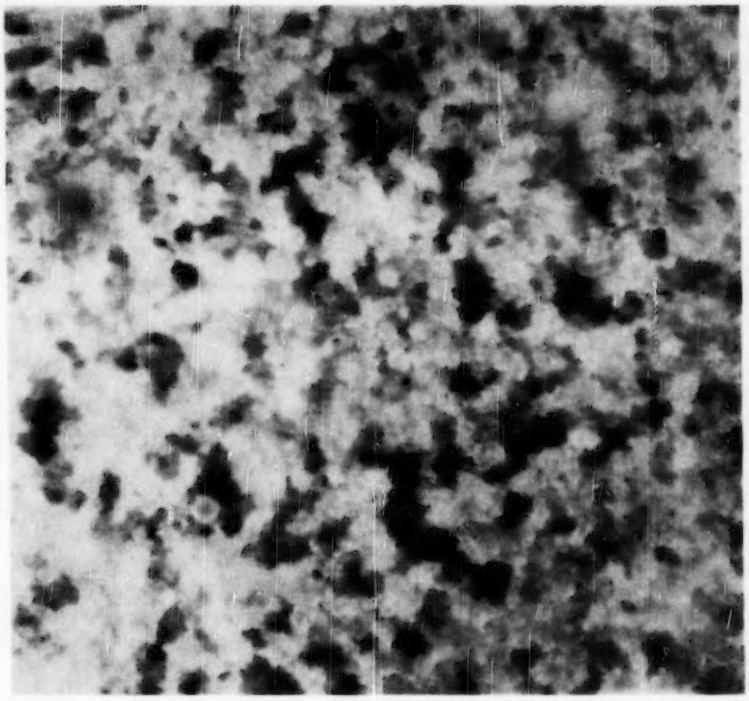


FIG. 1. *Photomicrograph of a coating which had been dissected horizontally, showing pore structure of the coating.*

pores be large or small. However, a trend could be noted toward a greater moisture-vapor transfer in those coatings having a large number of small pores.

While the moisture-vapor transfer was not influenced too greatly by the pore size, such was not the case with the hydrostatic-head property. Examination of Graph 3, which is a plot of pore size *vs.* hydrostatic head, clearly indicates a steady increase in the hydrostatic-head resistance as the pore size decreases. This graph also shows no appreciable increase in hydrostatic head until a pore size smaller than 30 μ is attained. This probably explains the loss in hydrostatic-head resistance in the mechanically or electrostatically perforated coated fabrics.

Having established the requirements necessary to obtain a high rate of moisture-vapor transfer as well as excellent hydrostatic-head resistance, the task remained to select the pigment best suited for the job. It will be noted, in observing the graphs, that each point as plotted is represented by a number. These numbers correspond to the pigment used in producing the coating, so that the point labeled (10) on each of the graphs represents properties obtained with a given pigment and the resultant coating. Close observation of these graphs will indicate that some pigments produce more desirable properties in the coatings than others do. For instance, pigment (11) gave a good moisture-vapor transfer, but a relatively low hydrostatic-head resistance, while pigment (19) gave a low hydrostatic-head resistance and a low rate of moisture-vapor transfer. However, a number of pigments—(1), (2), (3), (4), and (6)—gave coatings which had hydrostatic-head readings greater than 200 cm. of water and moisture-vapor-transfer values greater than 60% of the transmission rate of the base fabric. It will be noted that all these coatings contained surface pores smaller than 10 μ in diameter, although the number of pores varied widely.

While the good results obtained with pigments

(3), (4), and (6) might seem contradictory to the theory because of the small number of pores present, an explanation was found when the dissected coating was examined under the microscope. The photomicrograph (Figure 1) shows that the inner structure of the coating is not a simple one made up of vertical pores, but is, rather, a complicated three-dimensional structure of interconnected pores. Observation of the coatings indicated that this type of pore structure was much more prevalent in those coatings having the small-sized pores. Thus, through this interconnection within the coating, it was possible to transmit moisture vapor at a high rate even though there were wide variations in the number of surface pores.

Since a number of pigments were found which gave the desirable properties in this type of coating, the actual selection of the pigment was based on reproducibility on large-scale equipment, cost, ease of handling in the process, and the resulting physical properties of the coating.

Physical Properties and Testing

It was realized that, while the hydrostatic-head and moisture-vapor-transmission properties of the coated fabric were important considerations, the coating itself would have to exhibit certain other basic properties if it were to be of practical use. Among these were flexibility, flex-resistance, abrasion-resistance, resistance to ageing, and resistance to washing and/or dry-cleaning. Consequently, work was begun to build a practical coating compound using the solid pigment-synthetic rubber combination.

In the preceding section (Theory), it was determined that the resultant coating would have to be composed of a large volume of pigment bound together with a binder. Because the pigment volume plus the void volume in the dried coating was so large in relation to the binder volume, it was necessary to select a binder which had high strength. In addition, it was deemed important to have a coating which was flexible and resistant to solvents. Although a large number of binders were investigated, the requirements were such that an oil-resistant synthetic rubber was finally selected.

The choice of the pigment, as directed by the theory, became rather clear-cut. Of those pigments discussed in the Theory section, the one labeled (1) not only exhibited exceptional hydrostatic-head and moisture-vapor-transmission properties but also was low in cost, readily available, and lent itself to the process. This pigment was therefore chosen. Once the selection of the pigment and the rubber had been made, much time was spent in working out a compound which would have those physical properties which were desired.

TABLE II. PHYSICAL PROPERTIES OF FIELD-TESTED FABRIC (UNTREATED POROUS PIGMENT-SOLVENT CEMENT BINDER)

Hydrostatic head (cm. H_2O—ASTM (5th drop to penetrate))	249
Moisture-vapor transmission (% of that of base fabric (open-cup method))	59
Hydrostatic head (cm. H_2O) after 600 flexes (Chrysler flex machine)	180
Hydrostatic head (cm. H_2O) after 96 hrs. Weatherometer ageing	259
Taber abrader loss (g.) after 1,000 cycles using 500-g. weight and CS-8 wheels	0.230
Weight of coating (oz./yd.^{2})	3.1

In order to better understand the development of the final compound and its excellent physical properties, a backward glance must be taken to that stage of the development where an untreated porous pigment was being used with a synthetic-rubber binder. This combination, when used to produce a coated fabric, was then considered to exhibit such physical properties as to warrant durability field testing. Its properties, as measured in the laboratory, are given in Table II.

Field tests were arranged at the Quartermaster Board [2], Camp Lee, Virginia. The technique employed involved four phases—testing on the Rain, Obstacle, Glove, and Combat Courses. Impermeable and uncoated garments were run for comparison purposes along with the water-impermeable, water-vapor-permeable garments. It was desired to determine water-vapor permeability, durability of coating, and water-impermeability of the latter garments. The objective of the tests was to determine whether or not the experimental fabric had sufficient merit to warrant further development, and the field-test results were to serve as a guide in any resultant future work.

The results of these tests showed some deficiencies in the fabric. Examination of the tested experimental garments indicated that wherever leaking had occurred it was due to low abrasion- and flex-resistance of the coating.

The comments of the test subjects, pertaining to each phase of the test, and the statistical analysis obtained resulted in the recommendation that work be

continued on the experimental fabric, with especial emphasis being placed on toughening of the coating and improving the flexibility. In addition, it was suggested that in the future the portions of the test on moisture-vapor transmission and degree of comfort be conducted under closely controlled conditions, because the perspiration rate varied so much between individuals that a true evaluation was not possible in a general field test.

The faults in the experimental fabric, as determined by field testing, had to be corrected. In order to accomplish this, a number of more strenuous laboratory tests were needed, together with basic changes in the compound.

The field tests showed that the hydrostatic head of the coated fabric, as obtained with the ASTM tester on the aged and unaged fabric, was insufficient to meet the needs. In order to obtain a more strenuous hydrostatic-head test, the Suter machine was adopted as standard. An extension was added to this tester so that a maximum of 277 cm. of water pressure could be applied. In this test, water pressure is applied over 5 times the sample area of the ASTM tester, and the specimen is considered to have failed at the appearance of the first, rather than of the fifth drop. To fully test the coated fabric for waterproofness, the modified Suter test was run on the fabric in its original condition, after 96 hrs. of Weatherometer ageing, after 1,200 flexes on the Chrysler flex machine, and after 96 hrs. of Weatherometer ageing followed by 1,200 flexes on the Chrysler flex machine. When the fabric which had been field-tested was evaluated by these tests, the reason for leakage during the field tests was apparent. The Suter hydrostatic-head resistance of the fabric after Weatherometer ageing followed by flexing was extremely low.

The physical properties of the coated fabric as field-tested represented the optimum properties obtainable with the porous pigment-rubber binder combination at that stage of the development. However, simultaneous work being carried on with the solid pigment-rubber combination was at such a point as to show its superiority over the porous pigment in obtaining high hydrostatic-head resistance of the coated fabric. This combination also appeared to present more latitude in obtaining higher hydrostatic-head resistance since the pore size could be varied by the choice of pigment, whereas the pore size using the porous pigment was fixed.

Using the solid pigment-synthetic rubber combination discussed earlier in this section, it was found that the hydrostatic-head resistance of the coated fabric after ageing and flexing was superior to that obtained with the porous pigment-synthetic rubber combination. Since these hydrostatic-head values were still smaller than 100 cm. of water, concerted efforts were made to improve this property.

The thought occurred that possibly the hydrostatic-head resistance of the coated fabric might be raised if the angle of contact of the coating material were raised. In order to raise the angle of contact of the coating, it was necessary to incorporate into the coating some material having a higher angle of contact than the coating itself. Waxes, which are known to have a high angle of contact and to bleed to the surface of a rubber compound, seemed a logical choice. In addition, two other benefits could be seen as a result of the bleeding action of the wax. First, the pore diameter would be reduced by the film of wax, and, second, the ageing of the compound would be improved. This second benefit might have been of prime importance since examination of the theory and basic structure of the coating brought to light that possibly unusual ageing was taking place owing to the open nature of the coating. Addition of the wax to the basic compound confirmed the above thinking in that the coated fabric, after being aged and flexed, exhibited a hydrostatic-head resistance of well over 200 cm. of water.

At the same time that these improvements were being made in the compounding of the coating, investigations were undertaken to develop better coating techniques on various fabrics. Earlier work had shown that this type of coating could best be applied to tightly woven, fine-thread, water-repellent-treated fabrics. A weight-of-coating study was made on such a fabric, and it was found that when from 4.0 to 5.0 oz./sq.yd. of coating were applied, maximum physical properties were obtained. Fabrics with coating weights as low as 2 oz./sq.yd. showed reasonably good properties, while those with coating weights of 8 oz./sq.yd. or greater tended to crack when bent sharply with the coating out.

It was found that the coating was best applied to the fabric in a 3-coat operation—one tight coating, to anchor the coating to the fabric, and 2 coatings spread in opposite directions to completely cover the fabric. Attempts to reduce the number of coating operations gave spotty hydrostatic-head results because of incomplete coating around slubs and let-outs in the fabric.

Investigations have indicated that the coating can be successfully applied to one or both sides of the fabric and still retain high moisture-vapor-transmission rates. In addition to the tightly woven fabrics previously discussed, work has shown that excellent results can be obtained for such a fabric as sheeting. Here, in order to simulate fabric used in Army raincoats, a heavy coating was applied to one side of the fabric and a light coating to the other side. Actually, in order to attain properties equal to those of the higher-grade, 4.0 to 5.0-oz. one-side-coated fabrics, a heavier weight of coating was required (5.0 to 6.0 oz./sq.yd.).

During the entire development, it was recognized that the coated fabric would have to be cleaned by washing and/or dry-cleaning. The coated fabric finally developed does withstand 5 cycles of either of these cleaning methods, retaining a Suter hydrostatic-head of over 100 cm. of water.

As a result of the compounding studies and the improvement in coating techniques, it has been possible to produce on conventional rubber-spreader equipment considerable yardage of a water-impermeable, water-vapor-permeable coated fabric. A typical example of the data obtainable for this type of coated fabric is shown in Table III.

Examination of these data, along with those given in Table II, will show that not only have improvements been made in the waterproofness, both before and after ageing, but also the moisture-vapor-transfer rate has been increased considerably. Another property of prime importance is the abrasion-resistance. This has been increased more than two-fold. It was coated fabric of this type which was field-tested for comfort at the Quartermaster Climatic Research Laboratory, Lawrence, Mass.

Arrangements were made to conduct comfort tests on the coated fabric at the Army Quartermaster Corps Climatic Research Laboratory, Lawrence, Mass. J. W. Eliot, R. Bader, W. Goddard, and H. Hanson [3] carried on this work. The prime purpose of this work was to evaluate the moisture-transmitting properties of the coated fabric.

Three types of fabric, of the same approximate weight, were used in this evaluation. Parka-and-trousers assemblies were fabricated using the water-impermeable, water-vapor-permeable coated fabric, and, for control, assemblies were made from an impermeable coated fabric and an uncoated fabric. Additional clothing worn by the subjects was selected on the basis of being the most likely to be worn in the field, with the same climatic conditions prevailing.

TABLE III. TYPICAL PHYSICAL PROPERTIES OF A WATER-IMPERMEABLE, WATER-VAPOR-PERMEABLE FABRIC* (SOLID PIGMENT-SOLVENT CEMENT BINDER)

Weight of coating (oz./sq. yd.)	4.0
Hydrostatic head (cm. of water)	
Original	277+
After flexing, 1,200 flexes, Chrysler flex machine	277+
After O_3-bomb ageing, 96 hrs.	277+
After Weatherometer ageing, 96 hrs.	277+
After Weatherometer ageing for 96 hrs. and 1,200 flexes	277+
After creasing at −20°F	277+
After washing, 5 cycles	112
After dry-cleaning, 5 cycles	109
Moisture-vapor transmission (% of that of base fabric)	
Original	73
After washing, 5 cycles	75
After dry-cleaning, 5 cycles	75
Adhesion (lbs./2-in. width)	
Original	6.7
Flexibility (Clark softness), cm., at 70°F—Warp	9.8
—Filling	7.2
at 0°F—Warp	11.1
—Filling	8.6
After heat treatment, 5 hrs., at 220°F—Warp	10.1
—Filling	7.7
Abrasion-resistance	
Taber abrasion (g. loss), CS-8 wheels, 500-g. wt., 1,000 revolutions	0.100
Wyzenbeek (rubs), 6 lbs. tension, 3 lbs. pressure, 3/0 emery cloth	30
Blocking, 220°F, 30 min.	No blocking

* Fabric was 5.2-oz. water-repellent Byrd cloth coated on one side.

The tests were to simulate two separate field operations that might be encountered by individuals wearing parka and trousers. In these tests, the suits were used as: (1) a continuous-wear exposure suit —*i.e.*, a garment capable of remaining water impermeable should an aviator parachute into the sea, yet capable of transmitting perspiration from the aviator's clothing to maintain comfort during long periods of wear; and (2) a suit for use in wet-cold field conditions, where there is exposure to wetting from without and a high relative humidity which makes evaporation difficult from inside the garment.

In order to simulate those conditions prescribed, the climatic chambers during test were maintained at the following conditions: (1) temperate climate: temperature at 75°F and R.H. at 50%, with wind velocity at 3.0 miles per hr.; (2) wet-cold climate: temperature at 35°F and R.H. at 60%, with wind velocity at 3.0 miles per hr.

TABLE IV. BODY-PERSPIRATION TRANSMISSION, AS DETERMINED BY CLIMATIC TESTING

Climatic conditions	% Perspiration transmitted through garments made of: Impermeable coated fabric	Water-impermeable, water-vapor-permeable coated fabric	Uncoated fabric
75°F, 50% R.H.	56.2	84.5	85.4
35°F, 60% R.H.	43.4	64.9	65.6

Eight test subjects were conditioned by walking on a treadmill in the climatic chambers for 2 hrs. a day, 5 days a week, for 2 wks.

After conditioning of the test subjects, the tests were conducted with a rotation of garments among the subjects so that various sweat rates could be averaged out. In the temperate-climate experiments, the men were exposed for 5 hrs., exercising by walking on level treadmills at 3.5 miles per hr. for 10 min. and sitting quietly for the other 20 min. of each half-hour. In the wet-cold test, the test subjects were exposed for 2 hrs., walking continuously on treadmills at 3.5 miles per hr.

Physiological measurements were made to determine the body-weight change, moisture uptake of the garments, skin temperature, and rectal temperature. In addition, the test subjects' observations and suggestions were recorded. The body-weight change which was obtained by weighing the men nude before and after each exposure was used as an index of total sweat output. The moisture uptake was determined by obtaining the weight of each item of clothing before and after exposure. Skin temperatures were taken every 10 min. during the exposure by means of copper-constantan thermocouples attached to the skin. These thermocouples were read by a self-balancing recording potentiometer. The thermocouples were positioned as follows: (*a*) underside of terminal phalanx of great toe; (*b*) medial side of thigh, midway to knee; (*c*) abdomen, 2 in. lateral to umbilicus; (*d*) back, mid-line, at 7th cervical vertebra; (*e*) back of calf; (*f*) medial side of terminal phalanx of index finger. The rectal temperatures were also taken at 10-min. intervals and recorded in the same manner.

In their report on the tests, the authors [3] state:

"It is evident from body-weight losses, moisture absorption of the uniforms, and skin and rectal temperatures under these experimental conditions that the experimental semi-permeable material is far closer in its moisture-transmitting behavior to the control permeable material than to the control impermeable material. . . .

"Under both the wet-cold and temperate conditions, the average total sweat loss was less with the semi-permeable fabric than with the impermeable fabric. Inasmuch as sweat production by the body is quantitatively indicative of the heat load being imposed by clothing, it is fair to state that this difference represented a decrease of better than 60 calories in the heat load imposed on each man during the periods of exposure. It is calculated that the total heat production of each man, both in the 2-hr. wet-cold exposures and in the 5-hr. temperate exposures, approximated 600 to 700 calories. This means that the heat load saved by use of the experimental fabrics under these conditions represented (very roughly) 10% of the total load imposed."

The authors concluded: ". . . from a physiological point of view, standardization of rain suits or even continuous-wear exposure suits manufactured from fabrics containing the degree of vapor permeability found in the experimental fabric tested here is desirable."

Data in Table IV show exactly why the water-impermeable, water-vapor-permeable coated fabric can be considered to be very close in its ability to transmit moisture vapor to that of the uncoated fabric.

Conclusions

A coated fabric has been developed which is waterproof and simulates uncoated fabric in wearing comfort. This coated fabric has good flexibility, flex-resistance, abrasion-resistance, resistance to ageing, and resistance to washing and/or dry-cleaning. Field testing and controlled climatic testing have indicated the usefulness of this coated fabric.

Further developmental work is in progress in the application of this coated fabric to such end-items as tentage, sleeping-bag covers, raincoats, footwear, and other items in which the properties of waterproofness and the ability to transmit water vapor are desirable.

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The Place of Research in Textile Colleges

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The following article is the text of an address delivered by the author at the Anglo-American Conference on Textile Education held in Buxton, England, October 29–30, 1949. It is printed in the JOURNAL *because of reader interest in the programs being conducted in the several textile colleges, especially as they relate to textile research.*—Editor.

IN CONSIDERING the place of research in textile colleges, it should be made clear from the outset that, in my opinion, the primary objective of such institutions is educational. With this as a premise, then, it is necessary to consider the factors that have been introduced in the program of training young minds as they relate to educational requirements. Research is generally accepted as being one of these factors. It is felt by the textile colleges in America that research helps create an environment consistent with their recognized aim of providing technically trained personnel for the textile and allied industries.

There are a number of reasons why this philosophy has been adopted. First, and perhaps foremost, research has been encouraged in the textile colleges because of the salutory effect which such investigations have on the state of mind of both teacher and student. Research prompts numerous inquiries, and education can be more effective when an insatiable inquisitiveness has been created in the student's mind. It usually follows that an inquisitive mind is an open and eager mind. Those of us in the teaching profession know that our greatest challenge lies in the difficulty of transmitting information effectively or "putting the subject across." Excellent results in meeting this challenge are often experienced by the instructor when he describes the methods and results of his own research. Because of this, it frequently occurs that our best teachers are the ones who are conditioned by the spirit of research. Similarly, it

is easily recognized that students often do their best work when they are given individual assignments requiring independent thought. With this method, the assigned problem becomes more personal, and, with suitable catalytic action from the instructor, the laboratory experience of prosecuting a research project can be a most stimulating and worth-while assignment. Such a process invariably develops a keener sense of analysis, which should benefit the student in his subsequent work in industry.

Still another reason for subscribing to the important role research can play in education is the apparent need to develop an appreciation for research in the minds of the future industrial leaders. It has often been said in America that a wide gap exists between management and the research worker because the two do not speak the same language. One of my American colleagues, Dr. W. J. Hamburger, who visited in England last Spring, stated that this same situation appeared to exist abroad as well as in America. Further evidence of this condition in England is seen in an article published in the July *Proceedings* of the Textile Institute. Mr. H. A. Turner summarizes in part his paper on research as related to the Department of Textile Technology at Manchester by saying, "The full advantage of scientific and technological developments can only be secured for the textile producing industries if the personnel of the constituent firms includes a sufficient number of those able to understand fully the aims, methods, and results of scientific research. This number is not yet adequate." A number of attempts have been made to bridge this gap, but it seems more logical to employ methods in the colleges which will close this void than to try to straddle it. Certainly one technique that will prove useful is to develop in the student an understanding and a sense of value of just what research can accomplish, as well as its limitations. Psychologists have shown that there is no substitute for personal experience. The textile colleges have the unique opportunity through individual research assignments to develop the proper research point of view at an early stage in the lives of potential textile personnel.

Additionally, there is the obvious benefit that the textile industry receives in having textile problems investigated in its colleges. Much good work of direct application to the industry has resulted from these research programs. All one has to do to become convinced of this fact is to review the literature and make note of the amount of research emanating from the colleges that has been employed to advantage in improving methods and products in current use.

Having given some reasons why research is encouraged in the colleges, it appears pertinent to point out a few of the methods that have been employed in America in establishing research programs. Perhaps the most obvious is the one in which teaching staff members are permitted and encouraged to undertake research assignments of their own choosing. Such a practice presupposes three factors: first, a natural interest on the part of the staff member to do research; second, enough available time for him to undertake research; and, third, the necessary space and equipment which he may require. It is frequently found in my own college that, of these three ingredients, the second and third are often missing. Both of these factors are governed by economics and may raise stumbling blocks until sufficient funds are made available. This situation has become most acute in the postwar years, when, because of greatly increased enrollments, faculties are overloaded and every available square inch of space must be given over to the handling of students. In spite of this situation, however, when the first ingredient—namely, an interest in research—is present in excess, the staff member is generally able to keep some small research program functioning despite the other limitations. As a matter of fact, many colleges determine faculty promotions on the basis of research accomplishments in addition to the more universally accepted criterion of good teaching.

Another method which has been employed to encourage research is the establishment of research departments which are more or less independent of the teaching staff. This may appear to be a luxury at first glance, and it generally is in the initial stages. It has one very distinct advantage, however, in that there is continuity in the research effort. As a consequence, the program is usually conducted more efficiently and shows concrete results more quickly. From the point of view of subsidy, such an arrangement is admirably suited to support from government or industry because of the guaranteed man hours. With this help in getting started, research departments can often be made self-supporting in a relatively short period of time, and the introductory financial obligations are either diminished considerably or entirely eliminated. It has been found, too,

that, when their projects permit, these research workers make very valuable guest lecturers. Material presented in the classroom by this group is up-to-date and proves stimulating to the students. It is also found that having to give occasional lectures improves the efficiency of the research worker by forcing him to organize his thinking when he is presenting the results of his laboratory findings. If you will, it brings him down to earth.

My remarks up to this point have been confined to methods which are employed to encourage research at the faculty level. There are, in addition, several means available by which research can be accomplished at the student level. The first of these is the requirement prevalent in most colleges, whereby original or confirmatory research is required at the undergraduate level. To permit this, the curriculum is designed so that students have sufficient time to undertake to write theses in their final or senior year of undergraduate work. The projects in which this is done are generally short-term ones which can be completed in a relatively few hours. It is an unusual situation when such work is of far-reaching importance but, as stated earlier, such assignments help to create an appreciation for research in the student's mind. There is, as well, the accompanying benefit that the student must refer to the literature in his investigations and hence becomes better acquainted with the "state of the art." Excellent training also results from his having to comb the sources of information and thus become better informed on "what can be found where."

A similar plan is also employed at the graduate level—*i.e.*, beyond the bachelor's degree. The amount of research which a student can do increases and the quality improves as well at this stage, and many excellent studies have been made by graduate students to the benefit of the industry. The scheme just mentioned presupposes that the student is studying full time and has both the years for study and the necessary income available. There are many students, on the other hand, who have the time and, more important, the determination to continue their studies but lack the necessary funds. An interesting plan has been worked out to solve this dilemma which benefits both the student and the college. The main essential for its success is an appropriation in the school budget. Assuming that such a source of income exists, funds are established which permit desirable students to continue their studies on a part-time basis and to earn some income themselves during the balance of their time. There are many titles that have been adopted to describe such appointments—*e.g.*, "student instructor," "student assistant," "assistant instructor," "research fellow," "teaching fellow," "research assistant," or maybe just "assistant." These appointments are occasionally made on a competitive basis but more often are made at the discretion of a faculty committee. As mentioned earlier, this plan also assists the college in that these more mature students are available for laboratory assistance of a wide variety, ranging from dishwashing to actual laboratory instruction. There are also a number of colleges which use these graduate students as lecturers in the class room, although it is my opinion that this practice is dangerous.

There is at least one other advantage to this system. Those of us in educational work are constantly on the watch for potential staff members. Over and above the problem of competing with industry in terms of salary, there is the difficulty of trying to judge a man's teaching ability without first giving him an opportunity to show what he can do. By giving these graduate students an opportunity to do some "practice teaching" and observing them under varying conditions, it is usually possible to avoid placing round pegs in square holes.

A few words should also be said concerning the type of research conducted in the American textile colleges. I believe it would be safe to say that projects undertaken by either students or staff range from the most basic, academic type to the most practical, objective type. The nomenclature often used for these two classes is specific to the point of calling the former "fundamental research" and the latter "applied research." I might say that I do not subscribe to such delineation because in my opinion research is research at whatever level of practicability the work may be done. To be really frank about the matter, I believe it unwise to speak of fundamental research as divorced from other types of research unless one wants to call all research fundamental.

In order to make the picture a little clearer, I shall mention merely a few of the projects that have been undertaken in the textile colleges:

1. Studies of fiber fineness from the point of view of statistical distribution, methods of measuring fineness, and the effect of fineness on the spinning quality of fibers.

2. Various studies on the effect of twist on yarn and fabric properties.

3. Investigations of fabric structure and style from the consumer acceptance point of view.

4. Instrumentation studies of many different types, from testing instruments to control instruments for processing equipment.

5. Investigations on the various factors that affect uniformity of dyeing.

6. Evaluations of chemical assistants, such as wetting agents, detergents, lubricating oils, softeners, resins, and the like.

7. Developments of new processing equipment or special adaptations for existing machines.

8. Blending studies, from the point of view of both stock and color.

9. Studies of color-fastness to light, gas, liquids, and combinations of same.

10. Studies involving the chemical and physical makeup of fibers.

11. Processing studies involving new fibers, new equipment, new chemicals, and, in general, items new to the textile industry.

12. Market analyses, including methods and types of merchandising procedures.

A logical question that might be asked at this time is, "What is the source of funds which enables such research to be done by college faculty and students?" A few methods that have been employed to provide time and money have been referred to earlier. One is to allot sufficient funds in the college budget to permit light work loads for faculty members in order that they will have enough time for individual research. Similarly, work loads can be so designed that thesis supervisors are available for consultation and guidance at both the undergraduate and the graduate student level. Economically speaking, this is probably the cheapest method that can be employed to encourage research.

In many of the schools, administrative policies permit the acceptance of research assignments from outside agencies. These are, of course, subsidized by the sponsoring body and the salaries of the personnel may be underwritten either completely or in part, depending upon the nature and scope of the study. In some schools, the staff members are expected to work on projects of this type without compensation, while other schools augment salaries in proportion to the time which the individual puts in. Still other institutions hold such income as a fund to be distributed to all faculty members at a later date. In some isolated instances, projects are accepted by the schools without the expectation of any income whatsoever. These are looked upon as a public service and are justified on that basis.

Before World War II, most of the sponsored research in the schools came from the industry, trade, and scientific associations, as well as from philanthropically minded individuals and/or organizations. During and since the war, there has been a great deal of research conducted in our schools for government agencies. These assignments may emanate from branches of the armed forces or other departments of the government, such as the Department of Agriculture. Mention should also be made of the research sponsored by The Textile Foundation, a group sincerely interested in the improvement of textile education. I am sure that it is reasonably accurate to say that sponsored research is available for the textile schools at all levels and that the amount of work done is a function of the school's initiative and aggressiveness in contacting the appropriate parties.

In conclusion, I should like to sum up my comments as follows:

Although the main function of the textile colleges in America is "educational," in the generally accepted meaning of that term, research is looked upon as a very necessary adjunct to the training program. Such activity is carried on at both the student and the faculty level, either by direct or indirect subsidy. Programs are undertaken from a basic point of view and some may involve many years' work, while others, designed to yield certain specific answers to well-defined queries, may be of much shorter duration. In all cases, the textile colleges are attempting to meet the challenge given to them by industry—namely, the adequate training of personnel so that the industry will grow and prosper and be of greater service to mankind.

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Book Reviews

Handbuch der Färberei und anderer Prozesse der Textilveredlung. Vols. I and II. Albert Schaeffer. (In German.) Stuttgart, Konradin-Verlag Robert Kohlhammer, 1949. Vol. I, 638 + xx pages; Vol. II, 240 pp. Price, $18.00.

(Reviewed by L. Fusser, General Dyestuff Corporation, New York)

In this manual of dyeing the author has collected a vast amount of material about the application of dyestuffs in dyeing. In addition, enough data about the fibers and their conversion into fabrics, the mechanical and chemical finishing processes, and the dyestuffs are presented to give the reader a well-rounded view of textile chemistry and dyeing.

The work is divided into four volumes—a technical, a scientific, an experimental, and an analytical section—the first two of which are reviewed here. Both volumes are profusely illustrated with photographs and drawings, and the printing, paper, and binding are of good quality. The contents of the technical and scientific volumes are arranged in three main parts—the fibers, the dyestuffs, and the dyeing processes. The strict separation of the technical and scientific aspects of dyeing is based on the author's aim that his work should serve not only those engaged in the application of dyes but also many other persons in the textile and related industries who wish to gain some knowledge of dyeing either from the practical or theoretical point of view.

The first volume begins with a brief discussion of the origin, characteristics, properties, and principal uses of the most important textile fibers. A chapter on world production and consumption of fibers follows, based on old statistics which are out of date and therefore largely useless. The mechanical processes by which fibers are made into fabrics, the chemical processes involved in their preparation, bleaching, and finishing are clearly presented. No mention is made of the continuous-bleaching systems which are so widely used today. Little is said about the shrink-proofing of wool, while protection of wool against moth damage is dealt with rather amply. Likewise, creaseproofing of rayon and flame-resistant finishes could have been given a little more space.

The second part of Volume I discusses the nomenclature of commercial dyestuffs and their classification and gives a very comprehensive list of brand names of dyes and their manufacturers. Some discontinued brands and names of manufacturers out of business have been included. A discussion of the determination of fastness properties follows, based on the methods of the German fastness commission.

In the main part of Volume I the dyeing processes are treated very exhaustively in a manner similar to that employed in the dyeing manuals issued by the former I.G. Farbenindustrie; included are tables of suitable dyestuffs, mostly of European manufacture, and their properties. The dyeing of mixed materials is covered comprehensively, although the American reader will regret that nothing is said about mixed materials containing nylon. The author properly included a chapter about the fundamentals of water purification. The section that deals with dyeing machinery is systematically arranged and well illustrated. However, modern continuous-dyeing equipment, such as the pad-steam system and the Williams unit, is ignored. In fact, the author appears to be unaware of the progress which has been made in the United States in the continuous application of vat dyes.

A chapter on the drying of textiles, on the matching to shade, and a very extensive bibliography complete the first volume. Many American and British publications were not included in the bibliography, as, for example, Whittaker's *Dyeing with Coal Tar Dyes*, Horsfall and Lawrie's book on dyeing, the *American Cotton Handbook*, the *American Wool Handbook*, and others.

The second volume is devoted exclusively to the scientific aspects of fiber technology, dyestuff chemistry, and dyeing processes. Microscopy and physical structure of the more important textile fibers are covered, with excellent illustrations, except that of synthetic fibers only those on cellulose basis and Lanital are shown. The chemistry of the fibers is dealt with sufficiently to give an understanding of their molecular structure and chemical behavior. In this section, as also in the section about dyestuffs, the author fails to give references to the work of other investigators, although a long bibliography is

appended to each section. The chemistry of the dyestuffs is considered in relationship to their dyeing properties and the reactions that take place during the dyeing of the textile fibers. The dyestuffs are grouped according to the manner of application, and representative illustrations of each chemical type that falls within the group are given. When considering the direct dyes, some of the rules developed to explain substantivity on the basis of chemical structure are set forth.

The second volume is concluded with a critical discussion of the available experimental evidence which explains the chemical and physical reactions during the dyeing operations by which the various classes of dyestuffs are applied.

Summarizing, it may be stated that these two volumes are a welcome addition to the literature about dyeing. They would, however, be more useful to the textile colorist and dyer if there were more discussion of practical techniques and difficulties. Almost nothing is said about stripping of dyed material, a subject which cannot be neglected. The lists of dyestuffs and their uses, being heavily weighted with German and Swiss products, are of more value to the European than to the American colorist.

In spite of some of these shortcomings, a clear account of the dyeing of textile fibers is presented. These books should find their greatest usefulness in the hands of students in textile schools, laboratory as well as mill chemists, and all those persons in the textile and related industries who wish to acquire some technical or scientific information about the preparation and dyeing of the textile fibers; also, incidentally, about the fibers and the dyestuffs themselves and the rudiments of finishing.

American Cotton Handbook. Gilbert R. Merrill, Alfred R. Macormac, and Herbert R. Mauersberger. Second Edition. New York, Textile Book Publishers, Inc., 1949. 943 pages. Price, $9.50 ($10.50 outside U. S. and Canada).

(Reviewed by S. Jack Davis, Gallaway Mills Co., La Grange, Ga.)

Since the first edition of the *American Cotton Handbook* so ably fulfilled the aims of the authors—namely, to present an authoritative and concise reference work on all phases of the American cotton industry—this handbook is now well established in the textile field and one needs to note in the present review only the differences between the second edition and the first edition. The efforts of a single reviewer are necessarily inadequate because of the catholic coverage of material, much of which is beyond any one person's field of specialization.

The authors have wisely eliminated a chapter on cotton grey goods construction in the early edition, along with chapters on sewing thread, weaves, and the designing of cotton goods and terry fabrics, in order to provide space for more adequate attention to the latest advances in harvesting and processing the fiber, in bleaching, mercerizing, dyeing, and finishing.

The audacity of the authors in covering the entire field of carbohydrate chemistry in the space of 11 pages is somewhat amazing. What is even more surprising is that this terse review is pretty good. Nevertheless, one is inclined to question the compromise on this point, for such a succinct review will be of little assistance to the uninitiated, and unnecessary for the specialist, in understanding the later sections referring to modification of the fiber.

A similar difficult decision must have faced the authors in devoting a chapter to nomenclature of dyes.

The chapter on physical testing by Professor Schwarz is excellent. The chapter on chemical testing by Leo P. Sheehan likewise is able, although obviously not addressed to the layman, which is not essential in this case.

Reference to these two collaborating authors calls for a bouquet for the authors of this *Handbook* for utilizing the services of various specialists for specific contributions. Among these are Russell T. Fisher, President of the National Association of Cotton Manufacturers, who discusses the contribution of the cotton industry to World War II, and J. Roger Wallace, of the Commodity Research Bureau, who revised the chapter on the economic and statistical background of the industry.

The book is remarkably free of errors of omission or commission. The reviewer has spot-checked certain chapters of particular interest and finds that some relatively obscure but important facts are not omitted, even if they are only included in a literature reference. These references to the literature are especially helpful, as also is the detailed index of 42 pages. The presence of advertising is somewhat irritating, and the "educational value constituting excellent source material" of such advertising is questionable.

It is unnecessary to commend this *Handbook* to the textile technology fraternity; the scientist will find it satisfying and provocative—satisfying because a large number of related facts are so well organized, and provocative because its intrinsic conciseness sends one immediately to the appropriate reference literature.

The Principles of Rheological Measurement. Report of General Conference, British Rheologists' Club, Bedford College, University of London, October, 1946. Edinburgh and New York, Thomas Nelson & Sons, Ltd., 1949. 214 + x pages. Price, 30/—.

(Reviewed by Earl K. Fischer, National Bureau of Standards, Washington, D.C.)

This book is a collection of eleven papers presented at a conference on rheology held at the University of London in October, 1946, under the auspices of the British Rheologists' Club. Reports presented at a previous conference, held in 1944 under the same auspices, found their way into print under the title *Essays in Rheology*, published by Pitman in 1947 (reviewed in TEXTILE RESEARCH JOURNAL **18**, 134–5 (Feb. 1948)). The two volumes have some features in common: both seek to bring system into the physics of measurement of the "deformation and flow of matter"; both contain expressions of current views on research problems of great importance industrially and of vast complexity theoretically. With a field so broad and diverse, the present volume succeeds as a kind of topical progress report but it hardly justifies the ambitious title.

Some idea of the province claimed by rheology may be gained if we view flow in terms of viscometric units: the range is about 10^{25} poises and includes the "superfluid," liquid helium, at the one extreme and molten glasses and rocks at the other extreme. But this is a simplification, for the most interesting and perplexing examples of flow involve sundry other properties, including elasticity, variations in resistance to flow with rate of shear, yield points, etc. The authors in this volume concern themselves generally with the higher consistencies, and the papers deal with greases, pastes and doughs, rubber, wood, and metals. There is considerable emphasis on measuring methods, and a final chapter provides another disquisition into terminology. Most of the chapters are extended with contributed discussions of controversial and unresolved features of these measurements.

This book is not intended for the novice, but it will prove of great interest to the physicist and the physical chemist who themselves are grappling with the measurement of complex flow phenomena.

Temperature and Human Life. C. E. A. Winslow and L. P. Herrington. Princeton, N. J., Princeton University Press, 1949. 272 + xiv pages. Price, $3.50.

(Reviewed by Harwood S. Belding, Quartermaster Climatic Research Laboratory, Lawrence, Mass.)

Authors of books which synthesize information from different branches of science deserve special credit for their efforts in that they automatically forego the potential royalty opportunities which are open to successful writers of books organized to meet the needs of established college and professional-school courses in one branch of science. However, good books which cut across conventional fields of knowledge have been responsible for the establishment of new academic courses. That the recently published volume *Temperature and Human Life* represents a useful synthesis which might bring about such a result will be recognized by textile and clothing technologists, architectural engineers, climatologists, and biologists who have sought information as to the principles applicable in the protection of man against environmental stresses.

Drs. Winslow and Herrington were uniquely qualified for this task by reason of the large contribution which their laboratory, The John B. Pierce Laboratory of Hygiene, New Haven, Connecticut, has made toward establishing quantitatively the relationships between the comfort of man and the environmental factors of ambient temperature, radiation, and wind.

In highly technical contributions to the physiological and air-conditioning literatures, the Pierce Laboratory has established constants applicable for heat exchanges by convection, radiation, and evaporation of sweat. To elementary students of this subject these contributions must often have been unavailable or incomprehensible.

In *Temperature and Human Life*, the authors have used excellent judgment in making a readily understandable presentation of the basic principles which are applicable, while retaining enough quantitative information to meet many reference needs. Early

sections of the book are devoted to consideration of human heat production and loss, and adaptations of the body to hot and cold stresses. There follows an analysis of the problems of providing protection by means of clothing and housing. In conclusion, the influence of climate upon health is discussed.

Textile and clothing technologists whose interests lie in meeting clothing requirements for difficult environmental conditions will find the book valuable, both for its content and because of the large bibliography which is provided. The chapter "The Thermal Protective Influence of Clothing" will be of particular interest to them as an expression of the physiologist's viewpoint in making judgments of clothing adequacy.

Cotton Slashing. Paul V. Seydel. Published by *Textile Industries*, Atlanta, Ga., 1949. 270 pages. Price, $3.50.

(Reviewed by John W. Harrison, Bates Manufacturing Co., Lewiston, Maine)

Dr. Seydel has incorporated the series of articles on cotton slashing which aroused considerable interest when they appeared in *Textile Industries*, with an appendix of useful tables, into this résumé of the whys, whats, and hows of sizing. The volume shows a considerable background of information, and gives an excellent picture of the action of the various sizing materials and of their physical characteristics. Good chapters on frequent difficulties encountered and the descriptions of the conventional and hot-air slashers and new auxiliary equipment will be of interest to both students and workers.

Granted that this volume is intended for the practical man, the material on size preparation and testing is fairly complete. However, there is still room for a more complete discussion of the rheology involved. The research required to prepare such a chapter would be considerable, but a better statement of the problem and of known pertinent facts might prove valuable to many slashermen whose knowledge is limited now to the possibly biased information gleaned from size and equipment salesmen. Such a chapter might well help the nontechnical mill man to pick and choose among the materials and gadgets offered today in such a way as to considerably improve his work, or save money on useless gadgets and materials, or both.

Standards and Labels for Consumers' Goods. Jessie V. Coles. New York, Ronald Press Co., 1949. 556 pages. Price, $5.00.

(Reviewed by Ephraim Freedman, Macy's Bureau of Standards, New York)

The most comprehensive, analytical, and objective approach to the twin subjects of consumer-goods standards and informative labeling is to be found in *Standards and Labels for Consumers' Goods* by Jessie V. Coles.

Starting with consumer problems and attitudes, Miss Coles employs a thoroughly dispassionate yet forceful approach to the twin subjects by breaking them down into their basic components, describing the views of various segments—*i.e.*, manufacturer, retailer, advertiser, consumer, and educator—toward standards, informative labeling, and grade labeling.

Complete with clear-cut descriptions of an ever-increasing number of both voluntary and mandatory labeling and standards, replete with references, and generously seeded with pertinent observations, *Standards and Labels for Consumers' Goods* should become a standard text in all economics, merchandise, and advertising curricula.

Acetylene and Carbon Monoxide Chemistry. John W. Copenhaver and Maurice H. Bigelow. New York, Reinhold Publishing Corp., 1949. 357 + xvi pages. Price, $10.00.

(Reviewed by Martin H. Gurley, Jr., American Textile Co., Inc., Pawtucket, R. I.)

This book is based mainly on the chemistry of acetylene under pressure, as developed from the captured files of I.G. Farbenindustrie, the reports of the Field Information Agency, Technical (FIAT), the British Intelligence Objectives Sub-committee (BIOS), and the reports of the Publication Board of the U. S. Department of Commerce (PB Reports).

It is unfortunate that reliance on this literature has resulted in a minimum of references to the patent and periodical literature of Britain and the United States. This is particularly noticeable in the discussion of butadiene production.

The theoretical background is credited to Dr. Julius Walter Reppe, who initiated the book under the direction of the U. S. Army Chemical Corps after the fall of Germany.

The chapter headings are expressive of the contents of the book: I. Synthesis and Reactions of Acetylene at Atmospheric Pressure; II. Vinylation; III. Ethinylation; IV. Reactions of Products; V. Cyclopolyolefins; VI. The Chemistry of Carbon Monoxide-Carboxylation and Related Processes; VII. Synthesis and Reactions of Acetylene Homologs; VIII. Explosive Decompositions of Acetylene —Technique and Equipment for Handling Acetylene under Pressure Decomposition of Acetylene.

Many of the pressure reactions of acetylene are detailed as to quantities of materials and conditions of time, temperature, and pressure, making the book useful as a reference for those just starting in the field. In addition, Chapter VIII considers extensively the techniques of handling acetylene under pressure as well as the materials of construction and design of pressure vessels for such work.

The type is legible; the illustrations are satisfactory and the line drawings excellent. This reviewer noted no errors.

To the chemist interested only in textiles this book will probably be uninteresting. However, if the chemist should be desirous of obtaining knowledge about the origins of various resins and fiber-forming materials now widely used in textiles, this book will prove a valuable source of information.

A Handbook on Cotton Warp Sizing. Second Edition. A Publication of the Textile Research Staff of E. F. Houghton & Co. Philadelphia, Houghton Press, 1949. 160 pages. Price, $1.00.

(Reviewed by John W. Harrison, Bates Manufacturing Co., Lewiston, Maine)

This small volume is aimed at the apprentice and the practical slasherman. Containing, as it does, a review of the reasons for slashing and the common materials used in sizing as well as the equipment commonly encountered in the cotton slasher room, it provides a background source for the technical man who is interested in the sizing problem.

The *Handbook* is a revised edition of an earlier book by the same staff.

The discussion of the actual action of the size and of sizing techniques is rather elementary. There is very little material to help the student of rheology, although there are facts and charts which may aid mill men in understanding the phenomena which they have already observed.

Included are some typical sizing formulas and some tables of value to the production man. We believe this volume to have a limited usefulness, but the small cost may be well repaid if the individual reader receives help from any one of its various sections.

Diccionario Textil Panamericano. Compiled by J. Rodriguez Ontiveros. New York, Panamerican Publishing Co., Inc., 1949. 840 pages. Price, $15.00.

This Spanish-English, English-Spanish dictionary will fill a long-recognized need for an authoritative bilingual dictionary of technical terms common to the textile industries of Spanish- and English-speaking countries.

The vocabulary sections are exceptionally well organized and complete considering the fact that in many instances, especially in the Spanish-American countries, terms have arisen that are used only locally and that many equivalent terms are in use. The situation has been met by selecting the term most commonly used in the country of origin. In each case an abbreviation indicates the country in which the term is most frequently heard.

Words that are not usually found in standard English or standard Spanish dictionaries or terms that need definition to guide the reader in the choice of an equivalent are clearly defined.

An illustrated section comprising 285 pages devoted to textile technology and written in Spanish will serve as a useful handbook in Spanish-language countries. Fibers, mechanical operations, calculations employed in drafting, spinning, etc., and conversion factors are briefly discussed.

The volume has been a long time in preparation—six years, according to the preface—and, all-in-all, the care in its preparation is evident throughout. It can, without reservation, be recommended to all persons and organizations connected with the textile industry.

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